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Supporting Information

Donor–Acceptor Oligorotaxanes Made to Order

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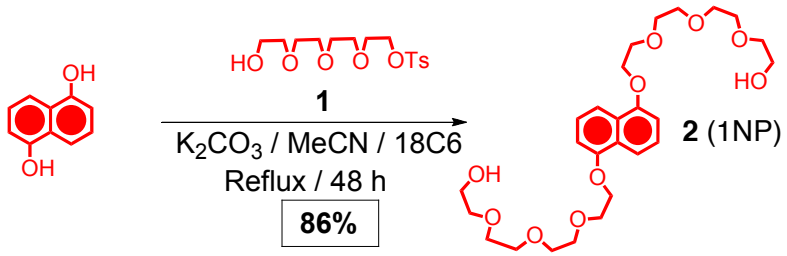
Experimental Section

1. General Methods

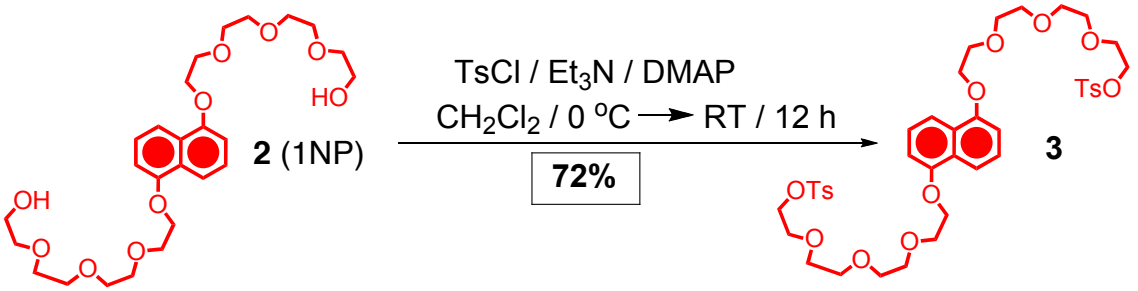
Starting materials and reagents were purchased from Aldrich or Fisher and used as received. Cyclobis(paraquat-*p*-phenylene) tetrakis(hexafluorophosphate)[S1] (CBPQT·4PF_6) monotosylated tetraethylene glycol[S2] **1**, and the alkyne-functionalized stopper precursor **5**[S3] were prepared following procedures already reported in the literature. All reactions were performed under an argon atmosphere and in dry solvents, unless otherwise stated. Analytical thin-layer chromatography (TLC) was performed on aluminum sheets, precoated with silica gel 60-F_{254} (Merck 5554). Flash chromatography was carried out using silica gel 60 (Silicycle) as the stationary phase. HPLC purification was performed on a preperative RP-HPLC instrument, using a C_{18} column (Agilent, 10μm packing, 30 mm × 250 mm) . The eluents used were MeCN and H_2O, both mixed with 0.1 % (v / v) trifluoroacetic acid (TFA). The detector was set to λ = 254 nm. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker Avance 500 MHz, or a Bruker Avance 600 MHz spectrometer at ambient temperature, unless otherwise noted. VT-NMR spectra were recorder on a Bruker Avance 600 MHz spectrometer and temperature-calibrated using neat MeOH (for T < 295 K) and ethylene glycol (for T > 295 K). Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents ($CDCl_3$: δ 7.26 ppm, CD_3CN: δ 1.94 ppm, $(CD_3)_2CO$: δ 2.05). High resolution electrospray ionization (HR ESI) mass spectra were measured on an Micromass Q-TOF Ultima mass spectrometer. Matrix assisted laser desorption and ionization – time of flight (MALDI-TOF) mass spectrometry were performed, using a Bruker Autoflex III instrument.

2. Synthetic Procedures



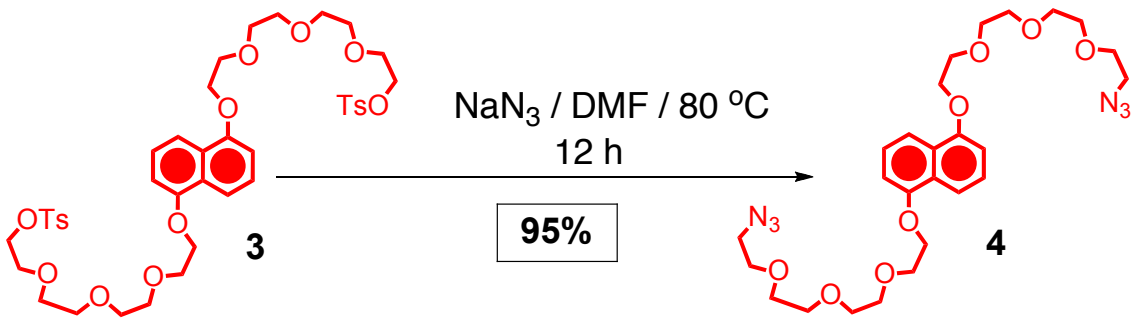
Scheme S1. The synthesis of the tetraethyleneglycol substituted DNP **2** (1NP), namely, 1,5-bis[2-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)ethoxy]naphthalene (BHEEEEN)

2: 1,5-Dihydroxynaphthalene (8.0 g, 49.9 mmol) was placed in a clean and dry round-bottomed flask with dry MeCN under argon. K_2CO_3 (17.13 g, 124.9 mmol) and 18-crown-6 (100 mg, 0.5 mmol) were added to the solution and it was heated under reflux for 1 h before monotosylated tetraethylene glycol[S2] **1** (43.5 g, 124.9 mmol) was added. The reaction mixture was refluxed under argon for 24 h and the solvent was removed thereafter under reduced pressure, before the reaction mixture was washed with H_2O and then extracted with small quantities, first of all with EtOAc and then with CH_2Cl_2. The organic layers were combined, dried (Na_2SO_4) and the solvent was removed under low pressure to yield the crude product, which was subjected to column chromatography [SiO_2: MeOH / EtOAc (5:95)]. The diol **2** was obtained as a reddish yellow oil (18.8 g, 86%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.85 (d, *J* = 8.4 Hz, 2H), 7.34 (t, *J* = 7.8, 2H), 6.83 (d, *J* = 7.7 Hz, 2H), 4.28 (t, *J* = 4.7, 4H), 3.98 (t, *J* = 4.9 Hz, 4H), 3.80–3.78 (m, 4H), 3.70–3.63 (m, 18H), 3.57–3.55 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ = 154.3, 126.6, 125.1, 114.5, 105.6, 70.6, 69.9, 67.8, 61.6 ppm. MALDI-TOF MS *m/z* calcd for 512.58; found 512.05 $[M]^+$.



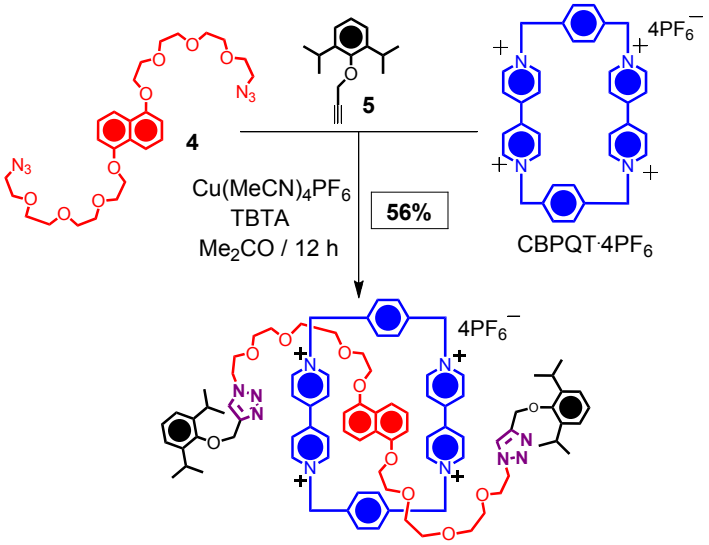
Scheme S2. The synthesis of the ditosylated BHEEEEN **3**

3: Et_3N (290 mg, 0.42 mL, 2.92 mmol) and *N, N*′- dimethylaminopyridine (DMAP) (120 mg, 0.97 mmol) were added to a solution of the diol **2** (500 mg, 0.975 mmol) in dry CH_2Cl_2 (50 mL) at 0 ˚C under a nitrogen atmosphere. After 5 min, a solution of *p*-toluene- sulfonylchloride (TsCl) (0.55 g, 2.92 mmol) was added directly to the reaction vessel. The reaction mixture was allowed to warm up to room temperature, before being stirred for an additional 12 h. The solvent was evaporated under reduced pressure, washed with H_2O, and then finally extracted into CH_2Cl_2 and dried (Na_2SO_4). The pure ditosylate **3** was obtained by performing column chromatography [SiO_2 : EtOAc] to yield the product as a reddish oil (570 mg, 72%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.62 (q, *J* = 5.1 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 4H), 6.60 (q, *J* = 5.1 Hz, 2H), 4.08-4.03 (m, 4H), 3.90-3.87 (m, 2H), 3.59–3.53 (m, 4H), 3.49–3.40 (m, 14H), 3.37–3.32 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ = 155.1, 144.9, 140.2, 132.9, 129.8, 127.6, 124.9, 114.5, 105.6, 70.7, 70.3, 69.2, 68.6, 67.8, 21.6 ppm. MALDI-TOF MS *m/z* calcd for $[M]^+$ 820.92; found 820.95.



Scheme S3. The synthesis of the 1NP diazide **4**

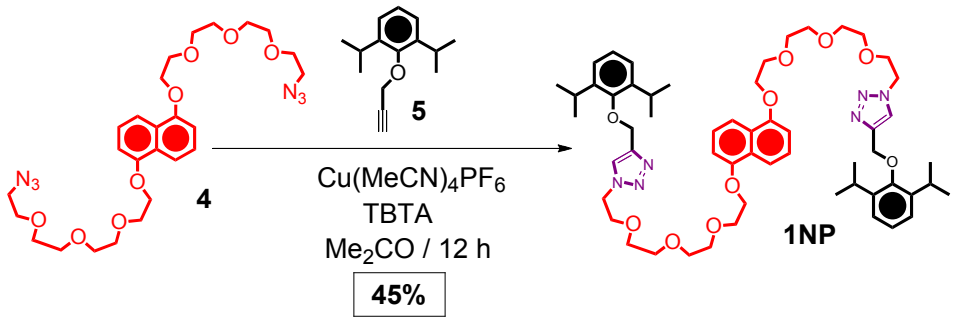
4: The ditosylate **3** (400 mg, 0.49 mmol) and NaN_3 (63 mg, 1.00 mmol) were dissolved in dry DMF (50 mL). The reaction mixture was heated to 80 ˚C for 12 h under a nitrogen atmosphere. The solvent was removed under vacuum and the reaction mixture was washed with H_2O to remove excess of the azide. The crude compound was extracted into CH_2Cl_2, dried (Na_2SO_4) and purified by column chromatography [SiO_2:EtOAc] to yield the monomeric diazide **3** as a yellow solid (261 mg, 95%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.85 (d, *J* = 8.47, 2H), 7.33 (t, *J* = 7.95, 2H), 6.83 (d, *J* = 7.82, 2H), 4.28 (t, *J* = 4.69, 4H), 3.98 (t, *J* = 5.06, 4H), 3.80–3.78 (m, 4H), 3.71–3.66 (m, 8H), 3.64–3.61 (m, 8H), 3.33 (t, *J* = 5.13, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ = 153.4, 125.8, 125.1, 113.4, 104.4, 70.1, 69.8, 69.1, 68.7, 49.6 ppm. MALDI-TOF MS *m/z* calcd for [M + Na]$^+$ 585.60; found 585.66.



Scheme S4. The synthesis of the 1NP rotaxane **[2]1NPR**·4PF_6

Synthetic Approach to the Preparation of the 1NP-Rotaxane: The diazide **4** (50 mg, 0.040 mmol) was placed in a round-bottomed flask (100 mL) and dissolved in dry Me_2CO under a nitrogen atmosphere. CBPQT·4PF_6 (96 mg, 0.088 mmol), tris-(benzyltriazolylmethyl)amine (TBTA) (21 mg, 0.04 mmol), and the alkyne-functionalized stopper precursor **5** (19 mg, 0.088 mmol) were added to this solution and it was stirred for 1 h. The solution became deep purple, indicating the formation of the pseudorotaxanes. Finally, ($Cu(MeCN)_4PF_6$) (21 mg, 0.04 mmol) was added and the reaction mixture was stirred for 24 h at room temperature. The solvent was then evaporated and the resulting purple solid was purified by RP-HPLC (H_2O – MeCN / 0 →100 % in 55 min, λ = 254 nm) to collect **[2]1NPR**·4PF_6 (47 mg, 56%). ^{1}H NMR (600 MHz, CD_3CN, 233K): δ = 1.21 (d, *J* = 7 Hz, 24H), 2.22 (d, *J* = 8 Hz, 2H), 3.31 (br t, 4H), 3.47 (br s, 4H), 3.51 (br s, 4H), 3.70 (br s, 4H), 3.79 (br s, 4H), 3.98 (br s, 4H), 4.11–4.23 (m, 12H), 4.79 (s, 4H), 5.54 (d, *J* = 14 Hz, 4H), 5.63 (d, *J* = 14 Hz, 4H), 5.83 (m, 3H),

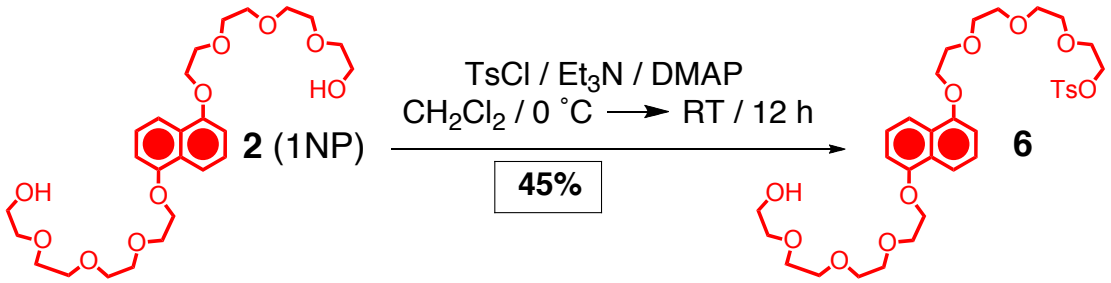
6.14 (d, J = 8 Hz, 2H), 7.34 (br d, 4H), 7.77 (s, 4H), 7.93 (br s, 2H), 7.94 (br s, 4H), 8.52 (d, J = 7 Hz, 4H), 8.96 (d, J = 7 Hz, 4H) ppm. ^{13}C NMR (125 MHz, CD_3CN, 295K): δ = 14.4, 23.1, 23.4, 24.3, 27.3, 30.1, 30.3, 32.6, 50.5, 65.9, 68.6, 69.6, 70.4, 71.0, 71.5, 72.0, 105.1, 109.3, 125.2, 126.0, 137.6, 142.9, 144.7, 146.1, 152.0, 153.7 ppm. ESI-HRMS *m/z* calcd for $[M-3PF_6]^+$ 553.6026; found 553.6029.



Scheme S5. The synthesis of the dumbbell compound **1NP**

1NP: The diazide **4** (20 mg, 0.013 mmol) was placed in a round-bottomed flask (100mL) and dissolved in dry Me_2CO (10 mL) under a nitrogen atmosphere. TBTA (2 mg, 0.007 mmol) and the alkyne-functionalized stopper precursor **5** (40 mg, 0.014 mmol) were added to the solution and it was stirred for 1 h. Finally, ($Cu(MeCN)_4PF_6$) (4 mg, 0.007 mmol) was added, and the reaction mixture was stirred for 24 h at room temperature. The solvent was then evaporated and the crude compound was extracted into CH_2Cl_2, dried (Na_2SO_4), and purified using silica gel column (SiO_2: EtOAc) to yield the dumbbell compound **1NP** as a yellow solid (24 mg, 45%). ^{1}H NMR (600 MHz, CD_3CN, 233K) δ = 7.96 (s, 2H), 7.67 (m, 6H), 7.25 (m, 6H), 7.09 (m, 6H), 6.74 (m, 6H), 4.73 (s, 4H), 4.41 (t, J = 5 Hz, 4H), 4.08 (br s, 10H), 3.79 (br s, 12H), 3.74 (t, J = 5 Hz, 4H), 3.60 (br s, 12H), 3.52 (br s, 8H), 3.47 (br m, 8H), 3.43 (br m, 4H), 3.37 (septet, J = 6.5 Hz, 4H),

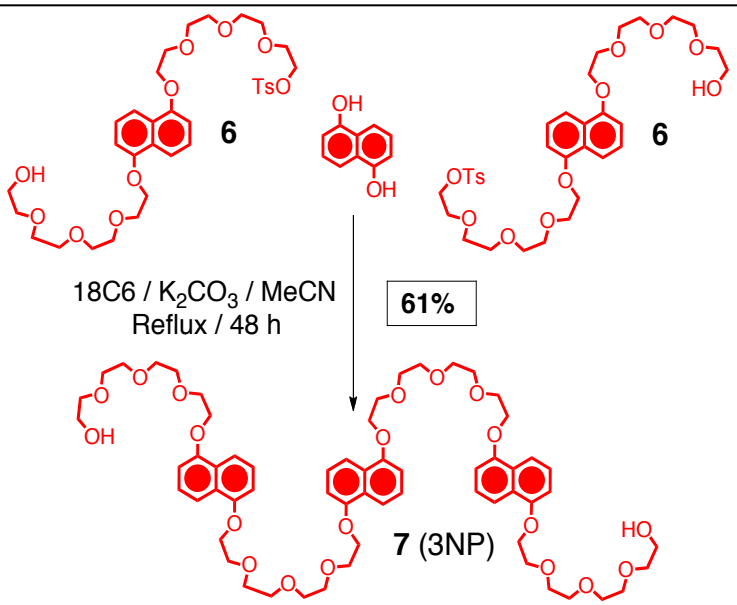
1.12 (d, J = 6.5 Hz, 24H) ppm. MALDI-TOF MS *m/z* calcd for $[M]^+$ 995.25; found: 995.26.



Scheme S6. The synthesis of monotosylated BHEEEEN **6**

6: Et_3N (880 mg, 1.22 mL, 8.77 mmol) and *N, N'*- dimethylaminopyridine (DMAP) (120 mg, 0.97 mmol) were added to a solution of the diol **2** (5.00 g, 9.75 mmol) in dry CH_2Cl_2 (200 mL) at 0 ˚C under a nitrogen atmosphere. After 5 min, a solution of *p*-toluene-sulfonylchloride (TsCl) (1.67 g, 8.77 mmol) in dry CH_2Cl_2 was added dropwise over a period of 1 h. The reaction mixture was allowed to warm up to room temperature, before being stirred for an additional 12 h. The solvent was evaporated under reduced pressure, washed with H_2O, and then finally extracted into CH_2Cl_2 and dried (Na_2SO_4). The pure monotosylate **6** was obtained by performing column chromatography [SiO_2 : EtOAc] to yield the product as a reddish oil (2.70 g, 45%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.62 (q, J = 5.1 Hz, 2H), 7.53 (d, J = 8.3 Hz, 4H), 6.60 (q, J = 5.1 Hz, 2H), 4.08-4.03 (m, 4H), 3.90-3.87 (m, 2H), 3.59–3.53 (m, 4H), 3.49–3.40 (m, 14H), 3.37–3.32 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ = 161.3, 144.9, 132.9, 129.8, 124.9, 114.5, 105.6,

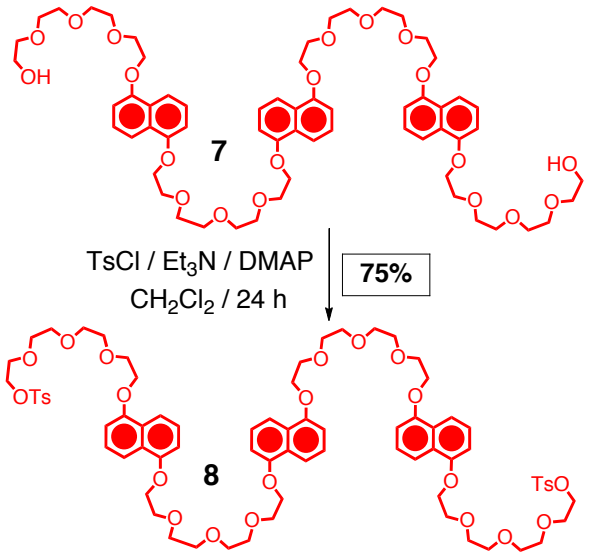
70.7, 70.3, 69.2, 68.6, 67.8, 61.7, 21.6 ppm. MALDI-TOF MS *m/z* calcd for $[M]^+$ 666.77; found $[M]^+$ 666.08.



Scheme S7. The synthesis of the DNP-trimer **7** (3NP)

7: 1,5-Dihydroxynaphthalene (400 mg, 2.52 mmol) was placed in a clean and dry round bottom flask, with dry MeCN under a nitrogen atmosphere. K_2CO_3 (760 mg, 5.54 mmol) and 18-crown-6 (100 mg, 0.25 mmol) were added to this solution and it was heated under reflux for 1 h before compound **3** (3.7 g, 5.54 mmol) was added and the reaction mixture was refluxed for a further 48 h. The solvent was removed under reduced pressure and the reaction mixture washed with H_2O and extracted into CH_2Cl_2. The organic layers were dried (Na_2SO_4) and the solvent was once again evaporated under reduced pressure to yield the crude compound. Pure **7** was obtained as a white powder following purification of the crude material, first of all by silica gel column chromatography [SiO_2: MeOH / EtOAc (15:85)], and then by RP-HPLC [H_2O – MeCN / 0 → 100 % in 55 min, λ = 254 nm] to obtain 1.2 g (61%) of the pure diol **7**. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ =

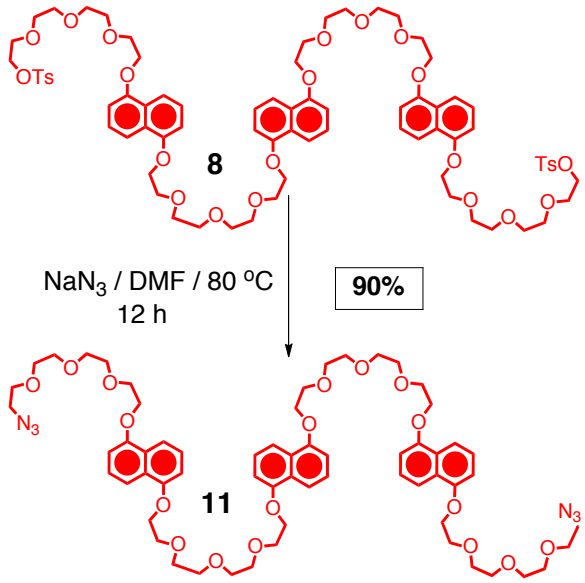
7.87–7.83 (m, 6H), 7.35–7.29 (m, 6H), 6.83–6.77 (m, 6H), 4.30–4.22(m, 12H), 4.00–3.95 (m, 12H), 3.81–3.77 (m, 12H), 3.73–3.64 (m, 26H), 3.59–3.56 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 160.1, 128.7, 123.5, 115.2, 105.6, 70.7, 70.3, 69.5, 62.8 ppm. MALDI-TOF MS *m/z* calcd for $[M + Na]^+$1172.30; found 1172.69 $[M + Na]^+$.



Scheme S8. The synthesis of the ditosylated trimer **8**

8: Et_3N (0.51 mL, 3.70 mmol) and DMAP (20 mg, 0.15 mmol) were added to a solution of the diol **7** (1.7 g, 1.48 mmol) in dry CH_2Cl_2 at 0 ˚C under a nitrogen atmosphere. After 5 min, solid *p*-toluenesulfonylchloride (710 mg, 3.70 mmol) was added directly to the reaction vessel. The reaction mixture was allowed to warm up to room temperature, before being stirred for 12 h. The solvent was evaporated under reduced pressure, the crude mixture washed with H_2O, then extracted into CH_2Cl_2 and dried (Na_2SO_4). The pure ditosylate **8** was obtained by column chromatography [SiO_2: EtOAc] yielding a

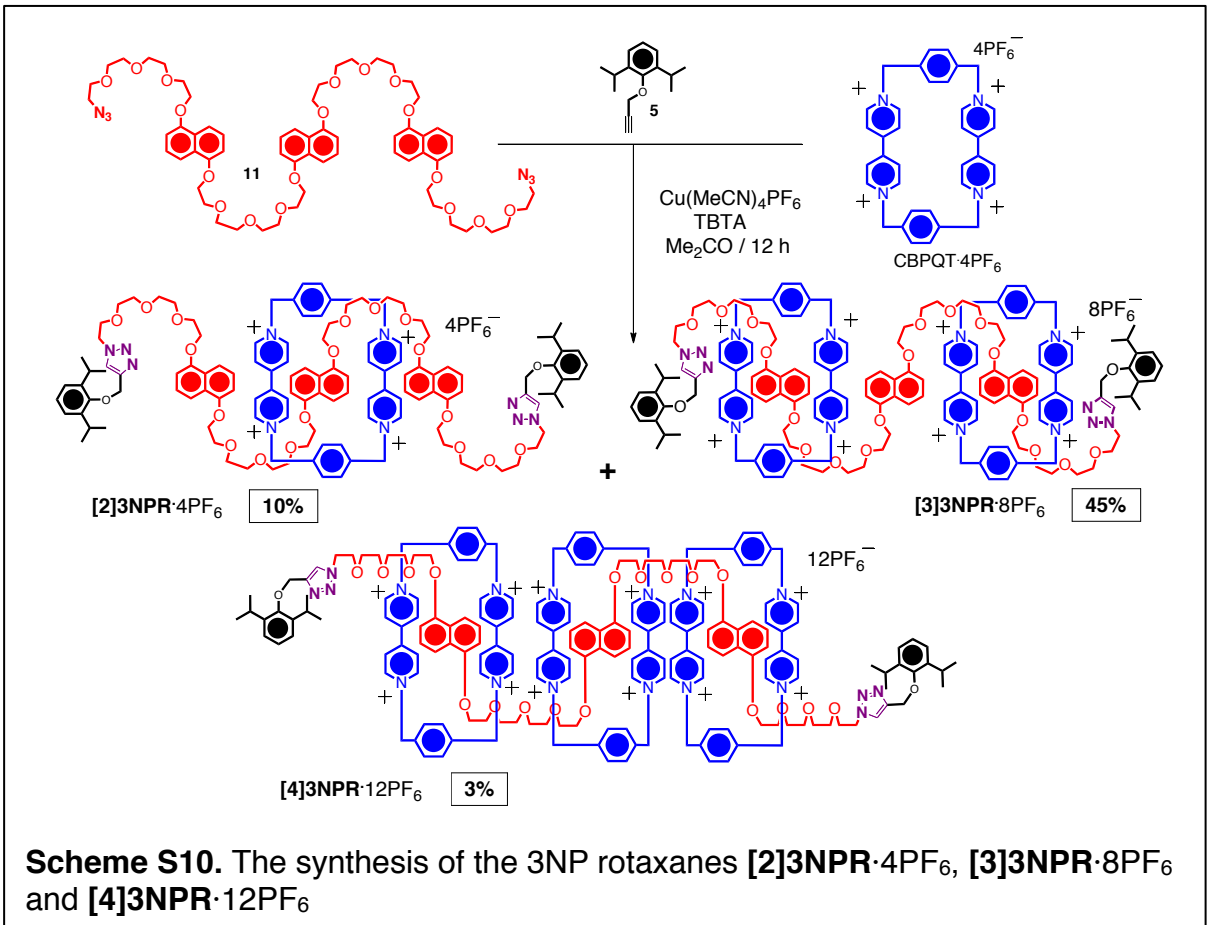
reddish oil (1.62 g, 75%). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ =7.87–7.82 (m, 6H), 7.77 (d, *J* = 8.46 Hz, 4H), 7.31 (m, 10H), 6.81–6.77 (m, 6H), 4.28–4.23 (m, 12H), 4.13-4.11 (m, 4H), 3.98–3.95 (m, 12H), 3.80–3.76 (m, 12H), 3.73-3.70 (m, 8H), 3.67–3.63 (m, 8H), 3.61–3.54 (m, 8H), 2.40 (s, 6H), ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 298 K): δ = 23.5, 68.3, 69.9, 70.16, 70.3, 70.4, 105.4, 113.8, 125.1, 128.1, 131.3, 141.7, 144.1, 144.4, 144.5, 157.9 ppm. MALDI-TOF MS *m/z* calcd for $[M + Na]^+$ 1480.68; found 1480.98 $[M + Na]^+$.



Scheme S9. The synthesis of the 3NP trimeric diazide **11**

11: The ditosylate **8** (840 mg, 0.56 mmol) and NaN_3 (200 mg, 0.17 mmol) were dissolved in dry DMF (100 mL). The reaction mixture was heated to 80 ˚C for 12 h under a nitrogen atmosphere. The solvent was removed under vacuum and the reaction mixture was washed with H_2O to remove excess of the azide. The crude compound was extracted

into CH_2Cl_2, dried (Na_2SO_4) and purified by column chromatography [SiO_2:EtOAc] to yield the trimeric diazide **11** as a yellow solid (500 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.78–7.74 (m, 6H), 7.26–7.20 (m, 6H), 6.74-6.67 (m, 6H), 4.21–4.13 (m, 12H), 3.93–3.85 (m, 12H), 3.73–3.68 (m, 12H), 3.65–3.58 (m, 15H), 3.57–3.53 (m, 8H), 3.25 (t, *J* = 5.21, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ = 154.2, 126.7, 125.0, 114.5, 105.5, 71.0, 70.8, 69.8, 67.8, 50.6 ppm.

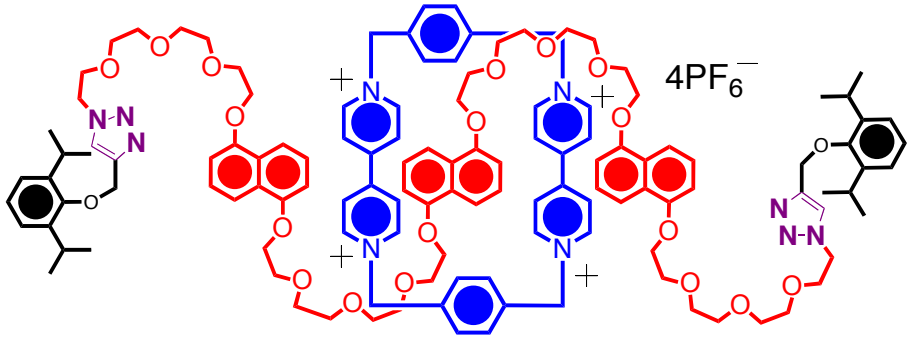


Scheme S10. The synthesis of the 3NP rotaxanes **[2]3NPR**·4PF_6, **[3]3NPR**·8PF_6 and **[4]3NPR**·12PF_6

General Synthetic Approach to the Preparation of the 3NP-Rotaxanes:

The diazide **11** (80 mg, 0.062 mmol) was placed in a round-bottomed flask (100 mL) and dissolved in dry Me_2CO under a nitrogen atmosphere. CBPQT·4PF_6 (22 mg, 0.20 mmol),

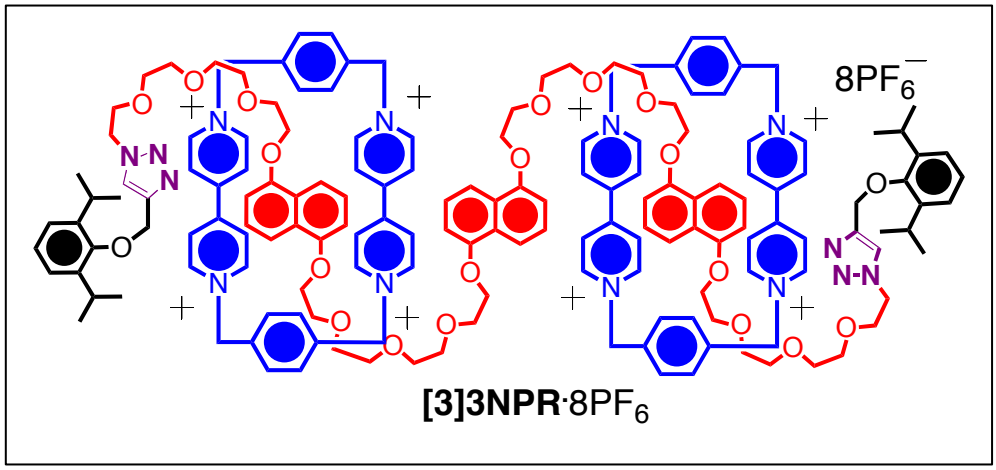
tris-(benzyltriazolylmethyl)amine (TBTA) (23 mg, 0.003 mmol), and the alkyne-functionalized stopper precursor **7** (29 mg, 0.14 mmol) were added to this solution and it was stirred for 1 h. The solution became deep purple, indicating the formation of the pseudorotaxanes. Finally, ($Cu(MeCN)_4PF_6$) (20 mg, 0.003 mmol) was added and the reaction mixture was stirred for 24 h at room temperature. The solvent was then evaporated and the resulting purple solid was purified by RP-HPLC (H_2O – MeCN / 0 →100 % in 55 min, λ = 254 nm). Three different fractions were collected, corresponding to **[2]3NPR**·$4PF_6$ (20 mg, 10%), **[3]3NPR**·$8PF_6$ (55 mg, 45%) and **[4]3NPR**·$12PF_6$ (15 mg, 3%).



[2]3NPR·$4PF_6$

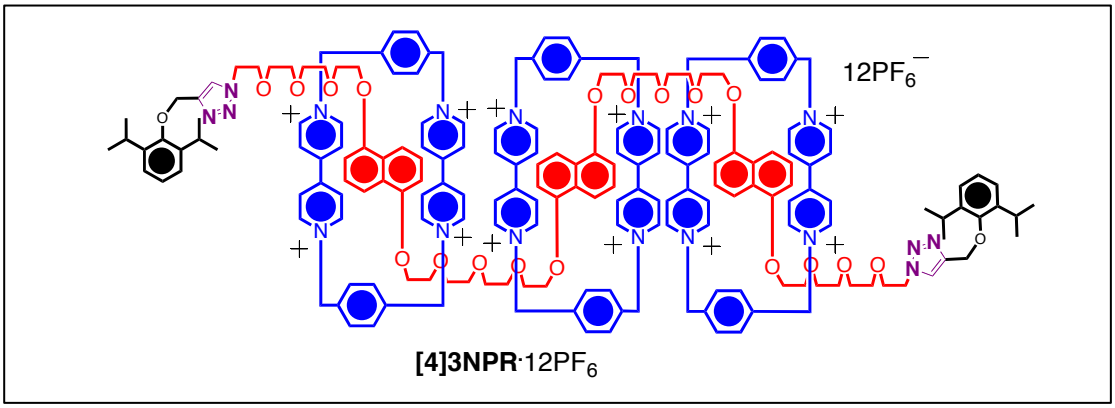
[2]3NPR·$4PF_6$: ^{1}H NMR (600 MHz, CD_3CN, 233 K): δ = 8.74 (d, *J* = 6.8 Hz, 4H), 8.13 (d, *J* = 6.6 Hz, 4H), 8.02 (s, 2H), 7.85–7.83 (b, 4H), 7.75-7.73 (b, 4H), 7.20 (b, 1H), 7.19 (b, 1H), 7.17 (d, J = 2.05 Hz, 2H), 7.16 (b, 2H), 7.14–7.16 (b, 3H), 7.05–6.98 (m, 6H), 6.57–6.54 (b, 4H), 6.52 (d, *J* = 7.3 Hz, 2H), 6.47–6.44 (b, 4H), 6.33 (d, *J* = 7.7 Hz, 2H), 5.84 (d, *J* = 8.5 Hz, 2H), 5.71 (d, *J* = 13.7 Hz, 4H), 5.58 (d, *J* = 8.5 Hz, 2H), 5.53 (d, *J* = 14.7 Hz, 4H), 4.80 (s, 4H), 4.52 (t, *J* = 4.7 Hz, 4H), 4.04–3.94 (b, 18H), 3.90–3.86 (b, 4H), 3.83–3.78 (b, 14H), 3.69–3.62 (b, 12H), 3.59–3.54 (b, 8H), 3.54–3.50 (b, 5H),

3.50–3.46 (b, 5H), 3.46–3.42 (b, 5H), 3.41 (m, 4H), 1.17 (d, J = 7.0 Hz, 24H) ppm. ^{13}C NMR (150 MHz, CD_3CN, 233K): δ = 154.2, 153.3, 141.7, 129.6, 126.2, 125.4, 124.3, 117.5, 114.0, 105.3, 72.6, 70.6, 70.4, 70.3, 70.1, 69.4, 67.6, 60.8, 26.2, 23.8 ppm. ESI-HRMS *m/z* calcd for $[M - PF_6]^+$ 2587.0296; found: 2587.0289; calcd for $[M - 2PF_6]^{2+}$ 1221.5343; found: 1221.5356; calcd for $[M - 3PF_6]^{3+}$ 765.7004; found: 765.7013.



[3]3NPR·8PF_6:^{1}H NMR (600 MHz, CD_3CN, 233 K): δ = 8.89 (d, J = 7.6 Hz, 4H), 8.78 (d, J = 7.5 Hz, 4H), 8.41 (d, J = 7.5 Hz, 4H), 8.13 (d, J = 7.5 Hz, 4H) 7.89 (s, 2H), 7.88 (b, 8H), 7.73 (d, J = 11.5, 8H), 7.19 (m, 2H), 7.18 (s, 2H), 7.16–7.13 (m, 2H), 7.03–7.00 (b, 4H), 7.00–6.95 (b, 8H), 6.92–6.84 (m, 4H), 6.84–6.80 (b, 4H), 6.25 (d, J = 7.5 Hz, 2H), 6.05 (d, J = 8.0, 2H), 6.00 (d, J = 7.5 Hz, 2H), 5.76 (d, J = 8.6 Hz, 2H), 5.70 (d, J = 8.6 Hz, 2H), 5.65 (d, J = 13.8 Hz, 4H), 5.57–5.52 (m, 8H), 5.46 (d, J = 14.4 Hz, 4H), 4.76 (s, 4H), 4.19 (t, J = 5.2 Hz, 18H), 4.15–4.05 (b, 16H), 3.99–3.96 (b, 4H), 3.95–3.91 (b, 4H), 3.89–3.85 (b, 4H), 3.80–3.75 (b, 8H), 3.68–3.61 (b, 12H), 3.57–3.52 (b, 4H), 3.51–3.48 (b, 4H), 3.45–3.38 (m, 8H), 1.18 (d, J = 7.0 Hz, 26H) ppm. ^{13}C NMR (150 MHz, CD_3CN, 233K): δ = 153.0, 152.3, 150.6, 144.2, 144.0, 143.3, 141.5, 136.1, 130.8,

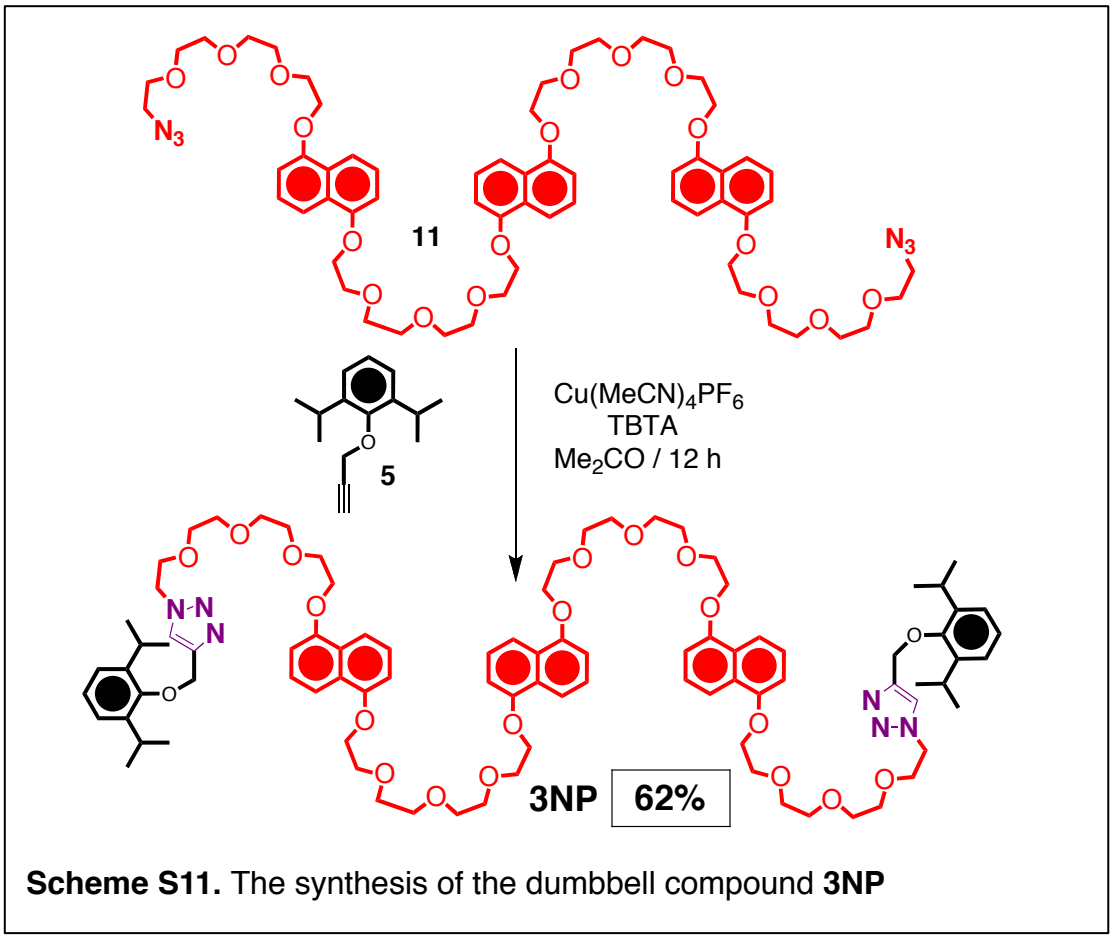
127.6, 125.4, 124.8, 123.8, 117.0, 113.4, 107.7, 105.5, 103.7, 70.6, 70.2, 70.0, 69.6, 69.2, 69.1, 68.8, 68.3, 67.8, 67.4, 64.5, 49.2, 29.5, 25.9, 23.0 ppm. ESI-HRMS *m/z* calcd for $[M - 2PF_6]^{2+}$ 1771.5939; found: 1771.5950; calcd for $[M - 3PF_6]^{3+}$ 1132.4068; found: 1132.4081; calcd for $[M - 4PF_6]^{4+}$ 813.0641; found: 813.0647; calcd for $[M - 5PF_6]^{5+}$ 621.4584; found: 621.4595.



[4]3NPR·12PF$_6$

[4]3NPR·12PF$_6$: ^{1}H NMR (600 MHz, CD_3CN, 233 K): δ = 8.97 (d, *J* = 7.1 Hz, 4H), 8.94–8.91 (b, 8H), 8.64 (t, *J* = 7.4 Hz, 8H), 8.53 (d, *J* = 7.1 Hz, 4H) 7.96–7.92 (m, 14H), 7.91–7.89 (b, 8H), 7.79–7.77 (b, 8H), 7.42–7.38 (m, 8H), 7.34–7.32 (m, 4H), 7.22–7.19 (b, 4H), 7.18–7.12 (b, 14H), 6.22–6.14 (m, 6H), 5.95–5.88 (m, 4H), 5.88–5.84 (m, 2H), 5.73–5.60 (m, 22H), 5.58–5.52 (d, *J* = 13.7, 4H), 4.78 (s, 4H), 4.26–4.12 (b, 28H), 4.06–3.96 (b, 22H), 3.81–3.77 (b, 4H), 3.71–3.68 (b, 4H), 3.53–3.49 (b, 4H), 3.49–3.42 (m, 4H), 3.37–3.32 (b, 4H), 2.28–2.22 (b, 6H), 1.20 (d, *J* = 7.0 Hz, 24 H) ppm. ^{13}C NMR (150 MHz, CD_3CN, 233K): δ = 156.9, 140.5, 132.1, 130.0, 125.0, 120.9, 118.1, 79.2, 43.7, 30.7, 28.4, 26.8, 24.4 ppm. ESI-HRMS *m/z* calcd for $[M - 2PF_6]^{2+}$ 2321.6558; found: 2321.6443; calcd for $[M - 3PF_6]^{3+}$ 1499.4492; found: 1499.4440; calcd for [*M* –

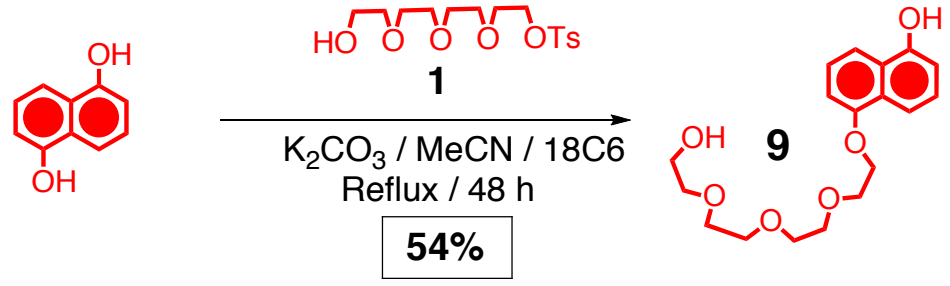
$4PF_6]^{4+}$ 1088.3459; found: 1088.3445; calcd for $[M - 5PF_6]^{5+}$ 841.6839; found: 841.6828; calcd for $[M - 6PF_6]^{6+}$ 677.2426; found: 677.2426.



Scheme S11. The synthesis of the dumbbell compound **3NP**

3NP: The diazide **11** (20 mg, 0.013 mmol) was placed in a round-bottomed flask (100mL) and dissolved in dry Me_2CO (10 mL) under a nitrogen atmosphere. TBTA (2 mg, 0.007 mmol) and the alkyne-functionalized stopper precursor **5** (40 mg, 0.014 mmol) were added to the solution and it was stirred for 1 h. Finally, ($Cu(MeCN)_4PF_6$) (4 mg, 0.007 mmol) was added, and the reaction mixture was stirred for 24 h at room temperature. The solvent was then evaporated and the crude compound was extracted into

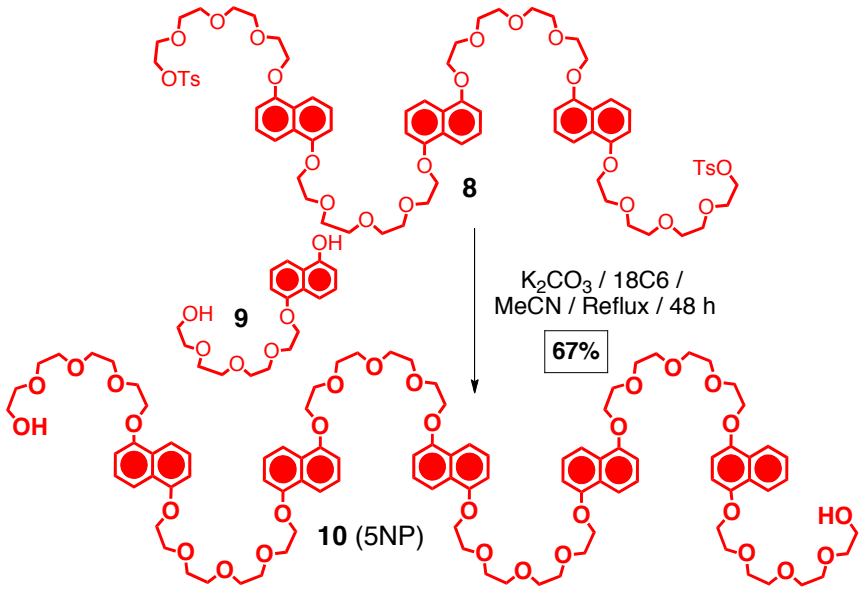
CH_2Cl_2, dried (Na_2SO_4), and purified using silica gel column (SiO_2: EtOAc) to yield the dumbbell compound **3NP** as a yellow solid (24 mg, 62%). ^{1}H NMR (600 MHz, CD_3CN, 233K) δ = 7.96 (s, 2H), 7.67 (m, 6H), 7.25 (m, 6H), 7.09 (m, 6H), 6.74 (m, 6H), 4.73 (s, 4H), 4.41 (t, *J* = 5 Hz, 4H), 4.08 (br s, 10H), 3.79 (br s, 12H), 3.74 (t, *J* = 5 Hz, 4H), 3.60 (br s, 12H), 3.52 (br s, 8H), 3.47 (br m, 8H), 3.43 (br m, 4H), 3.37 (septet, *J* = 6.5 Hz, 4H), 1.12 (d, *J* = 6.5 Hz, 24H) ppm. MALDI-TOF MS *m/z* calcd for $[M]^+$ 1631.98; found: 1631.96.



Scheme S12. The synthesis of the monofunctionalized DNP **9**

9: 1,5-Dihydroxynaphthalene (10 g, 62.4 mmol) was added to a dry round-bottomed flask and dry MeCN was added under nitrogen. K_2CO_3 (7.76 g, 56.19 mmol) and 18-crown-6 (120 mg, 6.24 mmol) were added to the reaction mixture and it was heated under reflux for 30 min. A solution of **1** (19.6 g, 56.19 mmol) in MeCN was added dropwise to the reaction vessel over a period of 1 h and the reaction was continued for an additional 12 h. The solvent was removed under vacuum, the crude material was washed with H_2O and organic layer was extracted in CH_2Cl_2. The crude product was purified by column chromatography [SiO_2: MeOH: EtOAc (5:95)] to yield a greenish yellow oil **9** (7.1 g, 54%). ^{1}H NMR (500 MHz, CD_3CN, 298 K): δ = 7.91 (d, *J* = 8.4 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.8, 1H), 6.88 (d, *J* = 7.7 Hz, 2H), 4.39 (t, *J* = 4.7, 2H), 3.98 (t, *J* =

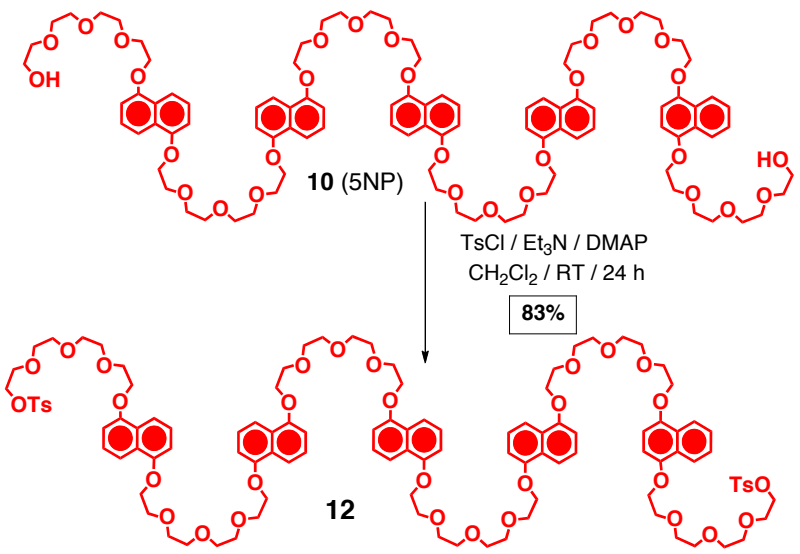
4.9 Hz, 2H), 3.76–3.74 (m, 2H), 3.70–3.63 (m, 8H), 3.49–3.51 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$ 298K): δ = 154.5, 153.9, 128.6, 126.7, 125.1, 114.5, 105.6, 70.6, 69.9, 67.8, 61.6 ppm. MALDI-TOF MS *m/z* calcd for $[M]^+$ 336.37; found 336.41.



Scheme S13. The synthesis of the DNP-pentamer **10** (5NP)

10: K_2CO_3 (60 mg, 0.43 mmol) and 18-crown-6 (10 mg, 0.02 mmol) were added to a solution of **9** (150 mg, 0.43 mmol) in dry MeCN, and the reaction mixture was heated under reflux for 30 min. A solution of **8** (250 mg, 0.17 mmol) in dry MeCN (100 mL) was added and the mixture was refluxed for an additional 36 h under a nitrogen atmosphere. The solvent was removed under reduced pressure, the crude mixture washed with H_2O and the organic layer extracted in CH_2Cl_2. Finally, it was dried (Na_2SO_4) and the crude product was purified by column chromatography [SiO_2: MeOH: EtOAc

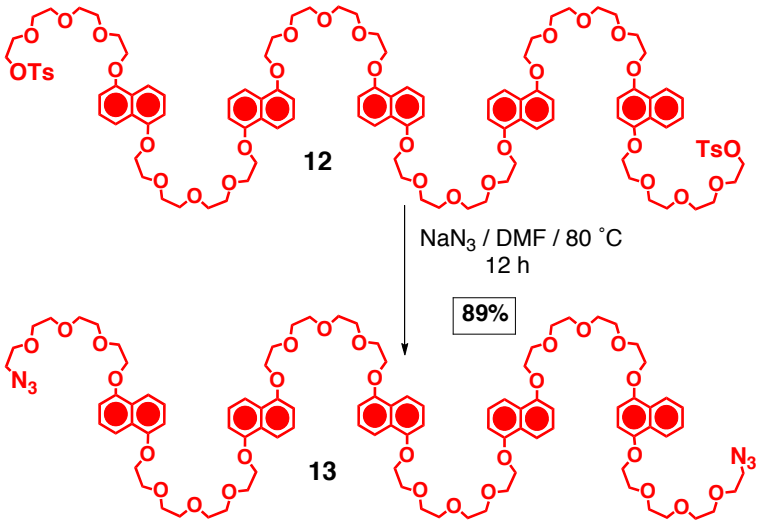
(15:85)] to yield the diol **10** as a yellow solid (170 mg, 67 %). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.84 (m, 10H), 7.31 (m, 10H), 6.79 (m, 10H), 4.30–4.22 (b, 20H), 4.00–3.94 (b, 20H), 3.82–3.76 (b, 21H), 3.74–3.64 (b, 36H), 3.58 (m, 6H) ppm**.** ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ = 154.3, 126.8, 125.0, 114.5, 105.6, 71.1, 69.6, 68.0, 61.7 ppm. MALDI-TOF MS *m/z* calcd for $[M + Na]^+$1809.03; found 1809.04.



Scheme S14. The synthesis of the 5NP ditosylate **12**

12: Compound **10** (170 mg, 0.096 mmol) was dissolved in dry CH_2Cl_2 and mixed with Et_3N (110 mg, 0.15 mL, 0.57 mmol) and DMAP (20 g, 0.01 mmol). The reaction mixture was stirred for 15 min at 0 ˚C under a nitrogen atmosphere. TsCl (110 mg, 0.57 mmol) was added to this solution and the reaction mixture was kept at room temperature for 24 h. After completion of the reaction, the solvent was removed under reduced pressure and the crude product washed with H_2O and extracted into CH_2Cl_2. After drying the crude product (Na_2SO_4) purification by column chromatography (SiO_2: EtOAc) yielded the

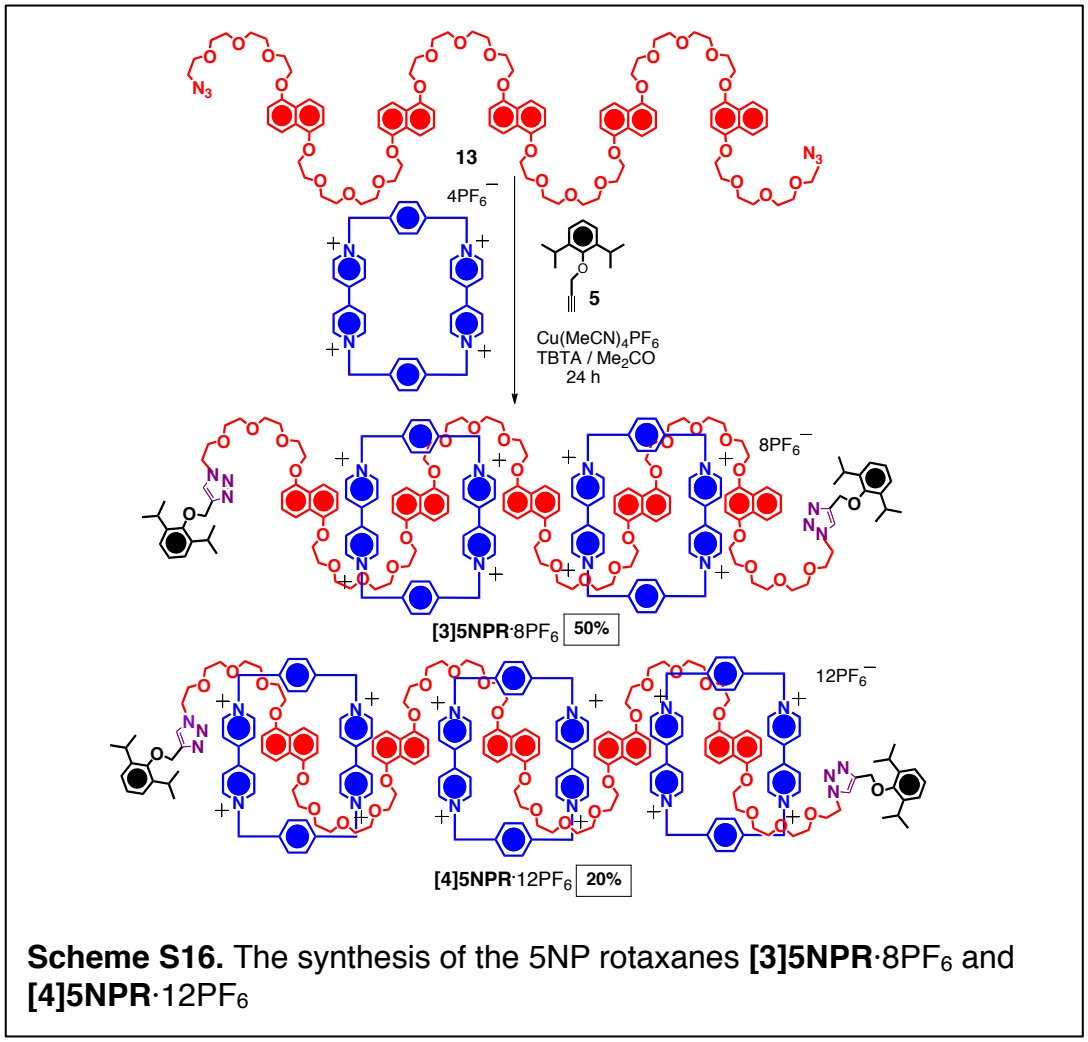
ditosylate **12** as a yellow oil (160 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.84 (m, 10H), 7.71 (d, *J* = 8.3 Hz, 4H), 7.34–7.28 (m, 14H), 6.82–6.78 (m, 10H), 4.28–4.22 (b, 20H), 4.14–4.10 (m, 10H), 3.89–3.94 (m, 20H), 3.80–3.75 (b, 19H), 3.73–3.69 (b, 15H), 3.567–3.63 (b, 10H), 3.60–3.54 (b, 10H), 2.41 (s, 6H) ppm**.** ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ = 154.7, 130.6, 128.7, 126.8, 125.5, 114.6, 105.8, 70.8, 69.8, 68.7, 21.5 ppm. MALDI-TOF MS *m/z* calcd for $[M + Na]^+$ 2117.40; found 2117.10.



Scheme S15. The synthesis of the 5NP pentameric diazide **13**

13: The ditosylate **12** (160 mg, 0.08 mmol) was dissolved in dry DMF (100 mL) along with NaN_3 (40 mg, 0.64 mmol). The reaction mixture was heated to 80 ˚C during 12 h under a nitrogen atmosphere. The solvent was removed under vacuum and reaction mixture was washed with H_2O to remove excess of the sodium azide. The crude product was extracted into CH_2Cl_2, dried (Na_2SO_4) and purified by column chromatography (SiO_2: EtOAc) to yield the bisazide **13** as a yellow solid (140 mg, 89%). ^{1}H NMR (500

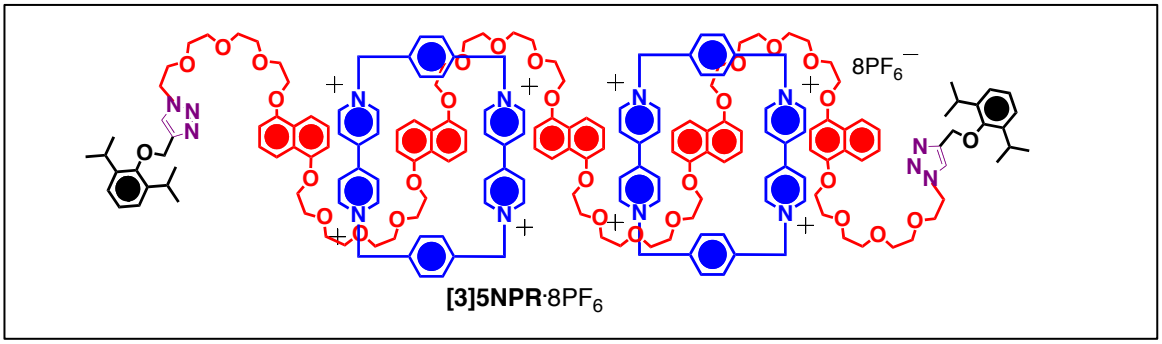
MHz, $CDCl_3$, 298 K): δ = 7.86–7.82 (m, 10H), 7.34–7.28 (m, 12H), 6.82–6.76 (m, 10H), 4.29–4.22 (m, 22H), 4.00–43.94 (m, 22H), 3.81–3.76 (m, 20H), 3.73–3.65 (b, 36H), 3.34 (t, *J* = 5.1, 4H) ppm**.** ^{13}C NMR (125 MHz, $CDCl_3$, 298K): δ = 156.9, 140.5, 132.1, 130.0, 125.0, 120.9, 118.1, 79.2, 51.2 ppm. MALDI-TOF MS *m/z* calcd for $[M + Na]^+$ 1859.06; found 1859.07.



Scheme S16. The synthesis of the 5NP rotaxanes **[3]5NPR**·$8PF_6$ and **[4]5NPR**·$12PF_6$

General Synthetic Approach to the Preparation of the 5NP-Rotaxanes: The diazide **13** (250 mg, 0.014 mmol) was placed in a round-bottomed flask (100 mL) and dissolved in dry Me_2CO (50 mL) under a nitrogen atmosphere. CBPQT·$4PF_6$ (39 mg, 0.035 mmol),

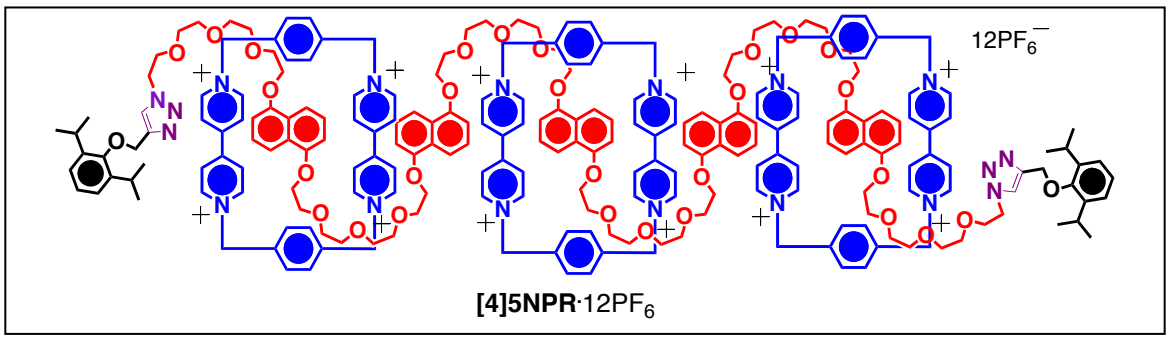
TBTA (2 mg, 0.007 mmol), and the alkyne-functionalized stopper precursor **7** (76 mg, 0.035 mmol) were added to the Me_2CO solution and the reaction mixture stirred for 1 h. It became deep purple, indicating the formation of the pseudorotaxanes. Finally, $(Cu(MeCN)_4PF_6)$ (3 mg, 0.007 mmol) was added and the reaction mixture was stirred for 24 h at room temperature. The solvent was then evaporated and the resulting purple solid was purified by RP-HPLC (H_2O – MeCN / 0 → 100 % in 55 min, λ = 254 nm). Two fractions were collected, namely the [3]rotaxane **[3]5NPR**·$8PF_6$ (15 mg, 50 %), and the [4]rotaxane **[4]5NPR**·$12PF_6$ (20 mg, 20 %).



[3]5NPR·$8PF_6$

[3]5NPR·$8PF_6$: ^{1}H NMR (600 MHz, CD_3CN, 233 K): δ = 8.94 (d, *J* = 7.1 Hz, 1H), 8.76–8.65 (b, 6H), 8.42 (d, *J* = 7.1 Hz, 1H), 8.23 (d, *J* = 7.2 Hz, 1H), 8.13–8.08 (b, 4H), 8.06 (d, *J* = 7.2 Hz, 1H), 8.01 (d, J = 5.9 Hz, 1H), 7.94–7.89 (b, 2H), 7.85–7.79 (b, 6H), 7.79–7.76 (b, 1H), 7.74–7.69 (b, 5H), 7.67–7.65 (b, 1H), 7.25–7.19 (m, 2H), 7.19–7.10 (b, 8H), 7.08–6.99 (b, 6H), 6.99–6.94 (b, 2H), 6.91–6.88 (b, 1H), 6.82–6.74 (b, 2H), 6.72–6.69 (b, 1H), 6.66–6.46 (b, 10H), 6.46–6.43 (b, 1H), 6.38 (d, *J* = 8.2 Hz, 1H), 6.34 (d, *J* = 8.2 Hz, 1H), 6.31 (t, *J* = 8.2 Hz, 1H), 6.15 (d, *J* = 7.9 Hz, 1H), 6.04 (d, *J* = 7.9 Hz, 1H), 5.98 (d, *J* = 7.9 Hz, 1H), 5.87–5.81 (b, 2H), 5.72–5.41 (b, 18H), 4.78 (d, J = 5.8 Hz,

2H), 4.73 (s, 2H), 4.54–4.49 (m, 2H), 4.19–3.74 (b, 54H), 3.69–3.37 (b, 41H), 3.38–3.34 (m, 2H), 1.20–1.12 (m, 24H). ^{13}C NMR (150 MHz, CD_3CN, 233K): δ = 153.5, 150.9, 148.1, 145.9, 144.8, 144.3, 143.8, 139.6, 137, 131.9, 131.3, 130.7, 130.4, 128.9, 128.1, 125.6, 124.5, 113.6, 70.0, 69.6, 67.6, 64.7, 63.1, 34.1, 33.4, 30.8, 23.6, 13.7 ppm. ESI-HRMS *m/z* calcd for $[M - 2PF_6]^{2+}$ 2088.7371; found: 2088.7172; calcd for $[M - 3PF_6]^{3+}$ 1344.1698; found: 1344.1646; calcd for $[M - 4PF_6]^{4+}$ 971.8862; found: 971.8871.

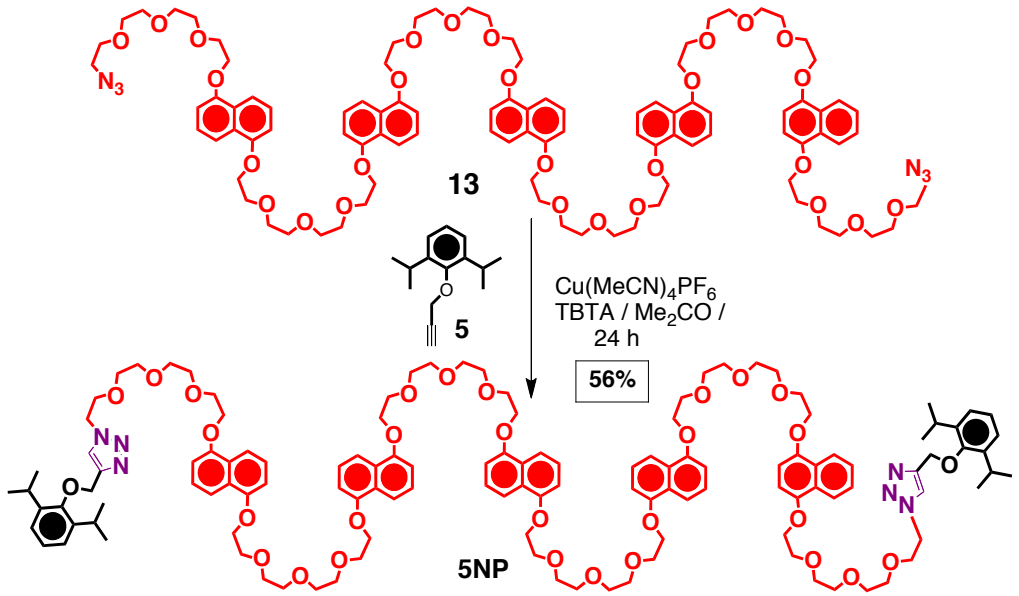


[4]5NPR·12PF$_6$

[4]5NPR·12PF$_6$: ^{1}H NMR (600 MHz, CD_3CN, 233 K): δ = 8.86 (d, *J* = 6.2 Hz, 4H), 8.74 (d, *J* = 6.2, 4H), 8.66 (d, *J* = 6.2 Hz, 4H), 8.38 (d, *J* = 6.2 Hz, 4H), 8.25 (d, *J* = 6.4 Hz, 4H), 8.08 (d, *J* = 6.2 Hz, 4H), 7.90 (s, 2H), 7.84 (s, 8H), 7.78 (s, 4H), 7.71 (s, 4H), 7.66 (d, *J* = 12.9, 8H), 7.20–7.13 (m, 7H), 6.96 (d, *J* = 5.6 Hz, 4H), 6.93 (t, *J* = 7.8, 8H), 6.83–6.75 (b, 8H), 6.73 (d, *J* = 8.4 Hz, 2H) 6.69 (d, *J* = 8.4 Hz, 2H), 6.53 (d, *J* = 5.6 Hz, 4H), 6.49 (d, *J* = 5.6 Hz, 4H), 6.16 (d, *J* = 7.3 Hz, 4H), 6.01 (d, *J* = 7.3 Hz, 2H), 5.96 (d, *J* = 7.3 Hz, 2H), 5.83 (d, *J* = 7.3 Hz, 2H), 5.73 (t, *J* = 7.3, 2H), 5.62–5.58 (m, 8H), 5.56–5.47 (m, 14H) 5.46–5.39 (b, 8H), 4.75 (s, 4H), 4.18–4.13 (b, 6H), 4.11–4.02 (b, 18H), 4.01–3.89 (b, 22H), 3.88–3.81 (b, 9H), 3.69–3.61 (b, 18H), 3.51–3.46 (b, 8H), 3.46–3.39 (b, 9H), 3.37–3.33 (b, 4H), 2.01 (d, *J* = 7.8 Hz, 2H), 1.86 (d, *J* = 7.8 Hz, 2H), 1.18 (d, *J* = 6.8 Hz, 24H). ^{13}C NMR (150 MHz, CD_3CN, 233K): δ = 156.1, 152.2, 148.1,

145.9, 144.8, 144.3, 143.8, 138.4, 131.9, 131.3, 130.7, 130.4, 128.9, 128.1, 125.6, 124.5, 113.6, 70.0, 69.6, 67.6, 64.7, 63.1, 35.3, 32.4, 29.2, 24.5 ppm. ESI-HRMS *m/z* calcd for $[M - 3PF_6]^{3+}$ 1710.8763; found: 1710.8693; calcd for $[M - 4PF_6]^{4+}$ 1246.9161; found: 1246.8966.

5NP: The diazide **13** (25 mg, 0.013 mmol) was placed in a round-bottomed flask (100



Scheme S17. The synthesis of the dumbbell compound **5NP**

mL) and dissolved in dry Me_2CO (10 mL) under a nitrogen atmosphere. TBTA (2 mg, 0.007 mmol), and the alkyne-functionalized stopper precursor **7** (40 mg, 0.014 mmol) were added to the solution and it was stirred for 1 h. Finally, ($Cu(MeCN)_4PF_6$) (4 mg, 0.007 mmol) was added and the reaction mixture was stirred for 24 h at room temperature. The solvent was then evaporated and the crude compound was extracted into CH_2Cl_2, dried (Na_2SO_4) and purified by column chromatography (SiO_2: EtOAc) to yield the dumbbell compound **5NP** as a yellow solid (20 mg, 56%). ^1H NMR (600 MHz, CD_3CN, 233K) δ = 7.96 (s, 2H), 7.68 (br d, 6H), 7.61 (br s, 3H), 7.27 (m, 10H), 7.10 (m,

6H), 6.74 (m, 10H), 4.74 (s, 4H), 4.42 (t, J = 4 Hz, 4H), 4.10 (br m, 24H), 3.81 (br s, 20H), 3.76 (t, J = 4 Hz, 4H), 3.62 (br s, 20H), 3.55 (br s, 18H), 3.49 (m, 8H), 3.45 (m, 4H), 3.37 (septet, J = 7 Hz, 4H), 1.13 (d, J = 7 Hz, 24H) ppm. MALDI-TOF MS *m/z* calcd for $[M]^+$ 2269.71; found: 2269.72.

3. Analysis of the ^{1}H NMR Spectra of the Rotaxanes

The rotaxanes **[2]3NPR**·4PF_6, **[3]3NPR**·8PF_6, **[4]3NPR**·12PF_6 based on the dumbbell **3NP** and the rotaxane **[4]5NPR**·12PF_6 utilizing the dumbbell **5NP** were characterized fully by ^{1}H NMR spectroscopy. Assignments of resonances to protons were confirmed by ^{1}H–^{1}H gDQF-COSY and ^{1}H–^{1}H gNOESY, recorded on a Bruker Avance 600 MHz spectrometer at 233K in CD_3COCD_3 or CD_3CN. A complete assignment in the slow exchange regime for the **[3]5NPR**·8PF_6 was not possible because of considerable line broadening associated with multiple dynamic processes occurring within the molecule on the ^{1}H NMR timescale. Based on previous investigations carried out on $CBPQT^{4+}$-containing compounds, the following protons were chosen as probes in order to determine the preferred (co-)conformations of the rotaxanes in solution: the α and β protons on the bipyridinium units on the $CBPQT^{4+}$ rings and the $H_{2/6}$ protons on the π-electron rich DNP units. In the absence of the guest (DNP units), the α and β protons associated with the $BIPY^{2+}$ units resonate as a couple of doublets (δ = 8.89 and 8.16 ppm) in CD_3CN at 233 K. When a $CBPQT^{4+}$ ring encircles a DNP unit, the α and β protons appear as four doublets on account of the local C_2 symmetry imposed on the $BIPY^{2+}$ unit by the DNP ring system.

3A. ^{1}H NMR Spectra of the Rotaxanes Recorded in CD_3CN at 233K

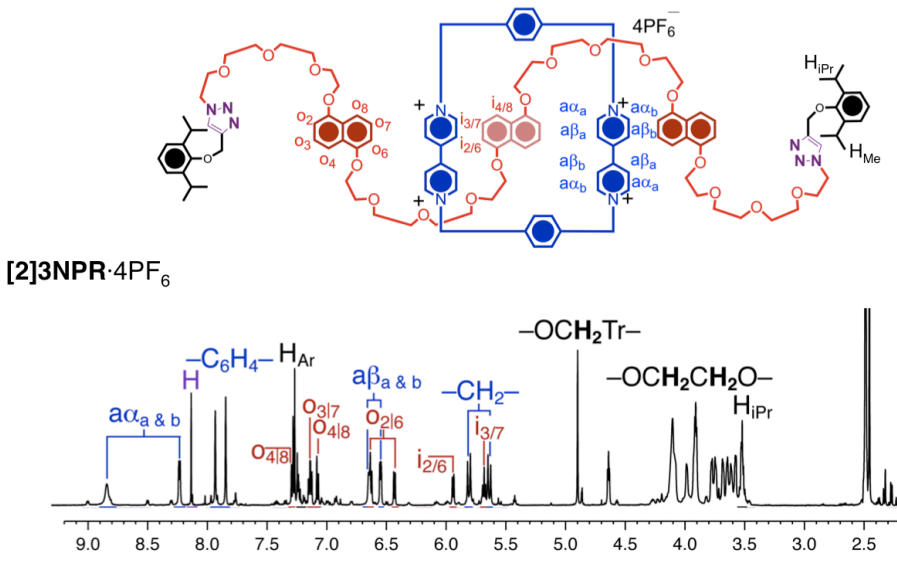


Figure S1. ^{1}H NMR Spectrum (600 MHz) of **[2]3NPR**·4PF_6 recorded in CD_3CN at 233 K

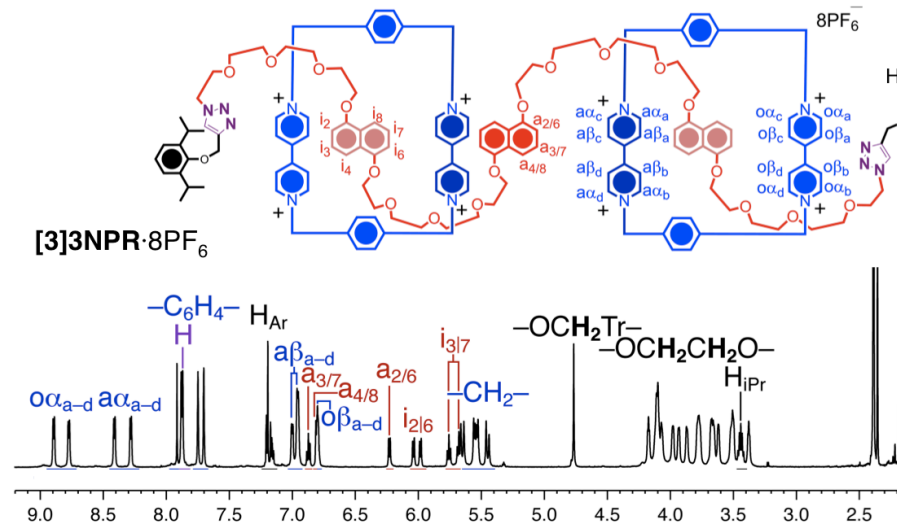


Figure S2. ^{1}H NMR Spectrum (600 MHz) of **[3]3NPR**·8PF_6 recorded in CD_3CN at 233 K

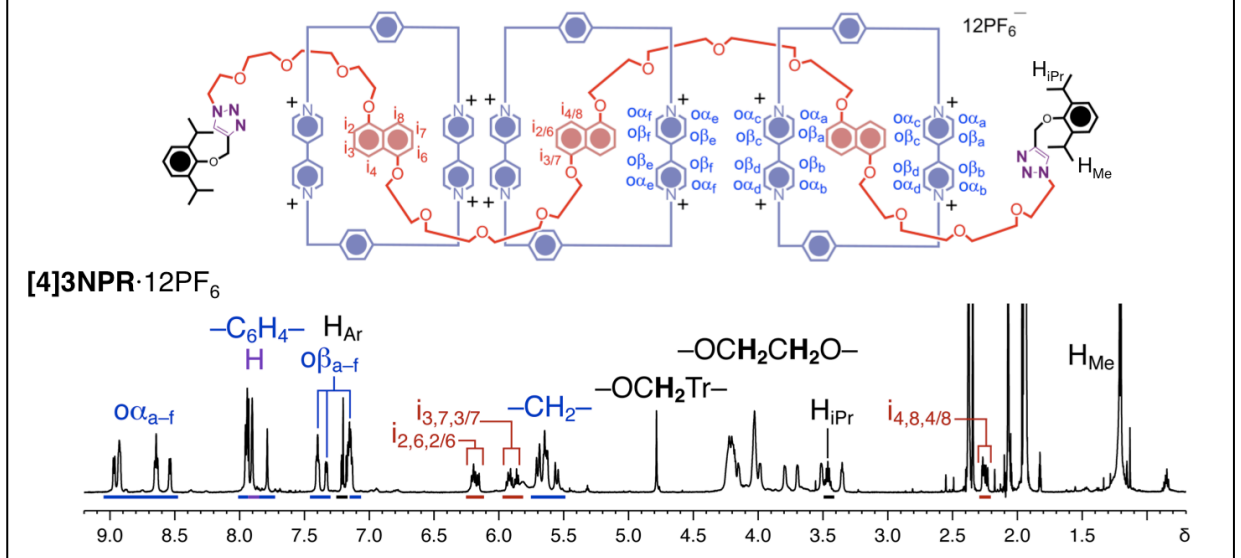


Figure S3. ^{1}H NMR Spectrum (600 MHz) of **[4]3NPR**·12PF$_6$ recorded in CD$_3$CN at 233 K

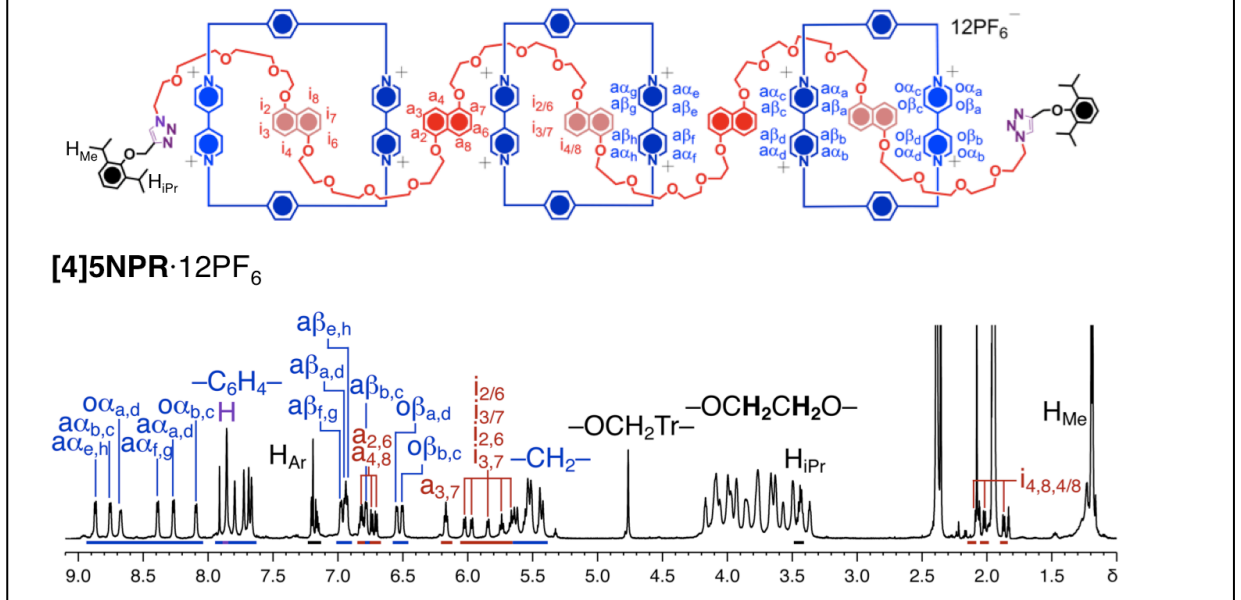


Figure S4. ^{1}H NMR Spectrum (600 MHz) of **[4]5NPR**·12PF$_6$ recorded in CD$_3$CN at 233 K

3B. Correlation Spectroscopy Performed on the Rotaxanes in CD_3CN at 233K

The ^1H-^1H gDQF-COSY of **[2]3NPR**·4PF_6 (Figure S5) in CD_3CN at 233K reveals correlation peaks between α and β protons of the $CBPQT^{4+}$ ring. The peaks for the protons $i_{3/7}$ and $i_{4/8}$ of the DNP unit which reside inside the π-electron deficient tetracationic cyclophane are visible as indicated by $i_{3/7} \leftrightarrow i_{4/8}$ in the spectrum. As expected, the $i_{4/8}$ is shifted upfield to the 2 ppm region because of an edge-to-face CH-π interaction with the bridging phenylene moieties in the $CBPQT^{4+}$ ring. The DNP protons $o_{3/7}$, which are not included in the cavity of the tetracationic cyclophane are also present, showing clear correlations with $o_{2/6}$ and $o_{4/8}$.

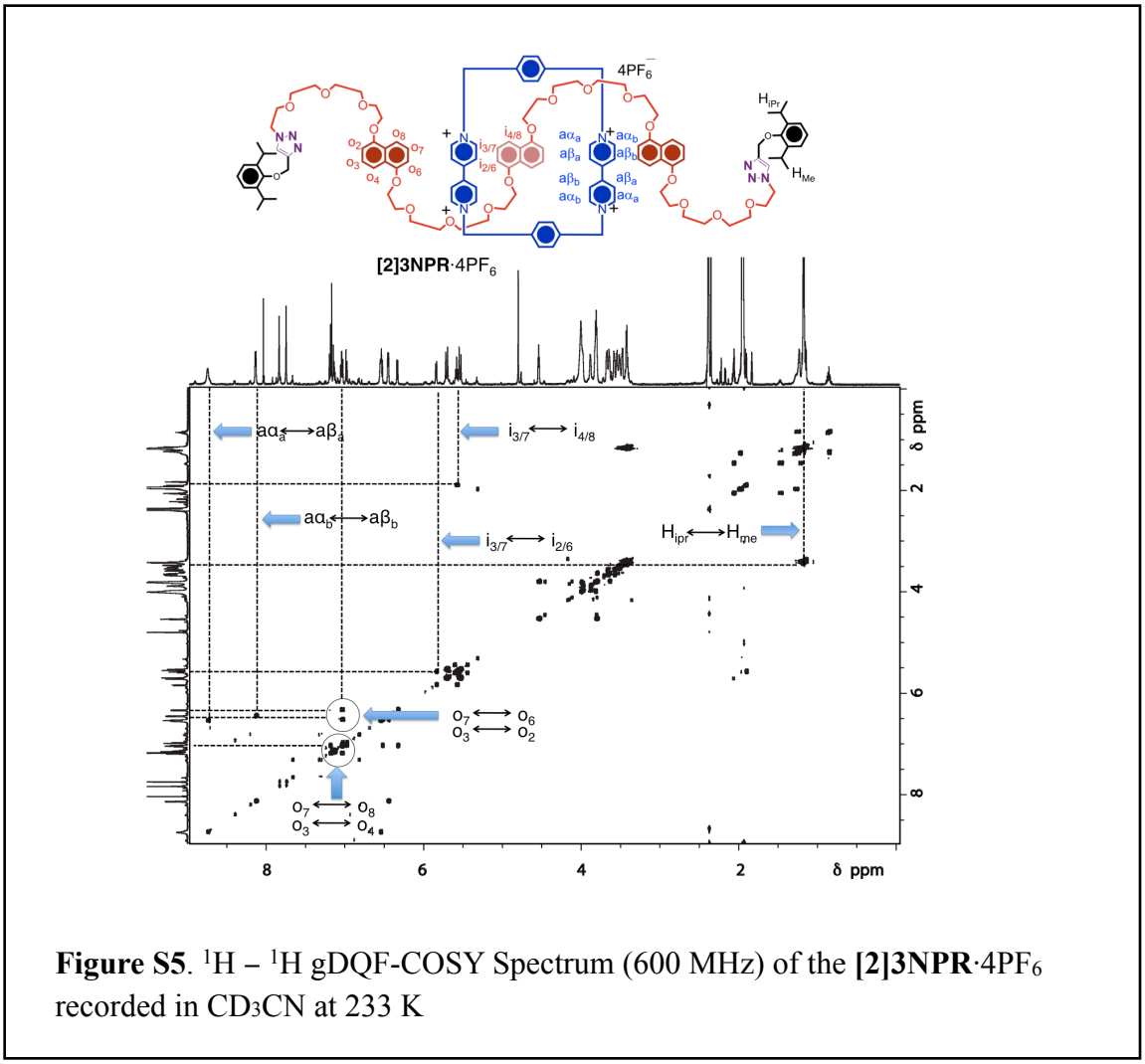


Figure S5. ^1H – ^1H gDQF-COSY Spectrum (600 MHz) of the **[2]3NPR**·4PF_6 recorded in CD_3CN at 233 K

The ^{1}H-^{1}H gDQF-COSY (Figure S6) of **[3]3NPR**·8PF$_6$ in CD$_3$CN at 233 K reveals strong correlation peaks between the α and β protons of the CBPQT^{4+} ring. Unlike **[2]3NPR**·4PF$_6$ (Figure S5), all the α and β protons are heterotopic (as denoted by oα, aα and oβ, aβ peaks respectively) COMEBACK. The correlation spectrum clearly demonstrates four different sets of both α and β resonances. The peaks for the protons $i_{2/6}$, $i_{3/7}$ and $i_{4/8}$ of the DNP units that reside inside the π-electron deficient tetracationic cyclophane are labeled in the spectrum. The DNP protons that are not included in the cavity of CBPQT^{4+} but have strong alongside interactions with the BIPY^{2+} units of the macrocycle ($a_{3/7}$, $a_{2/6}$ and $a_{4/8}$) are also present and labeled in the spectrum.

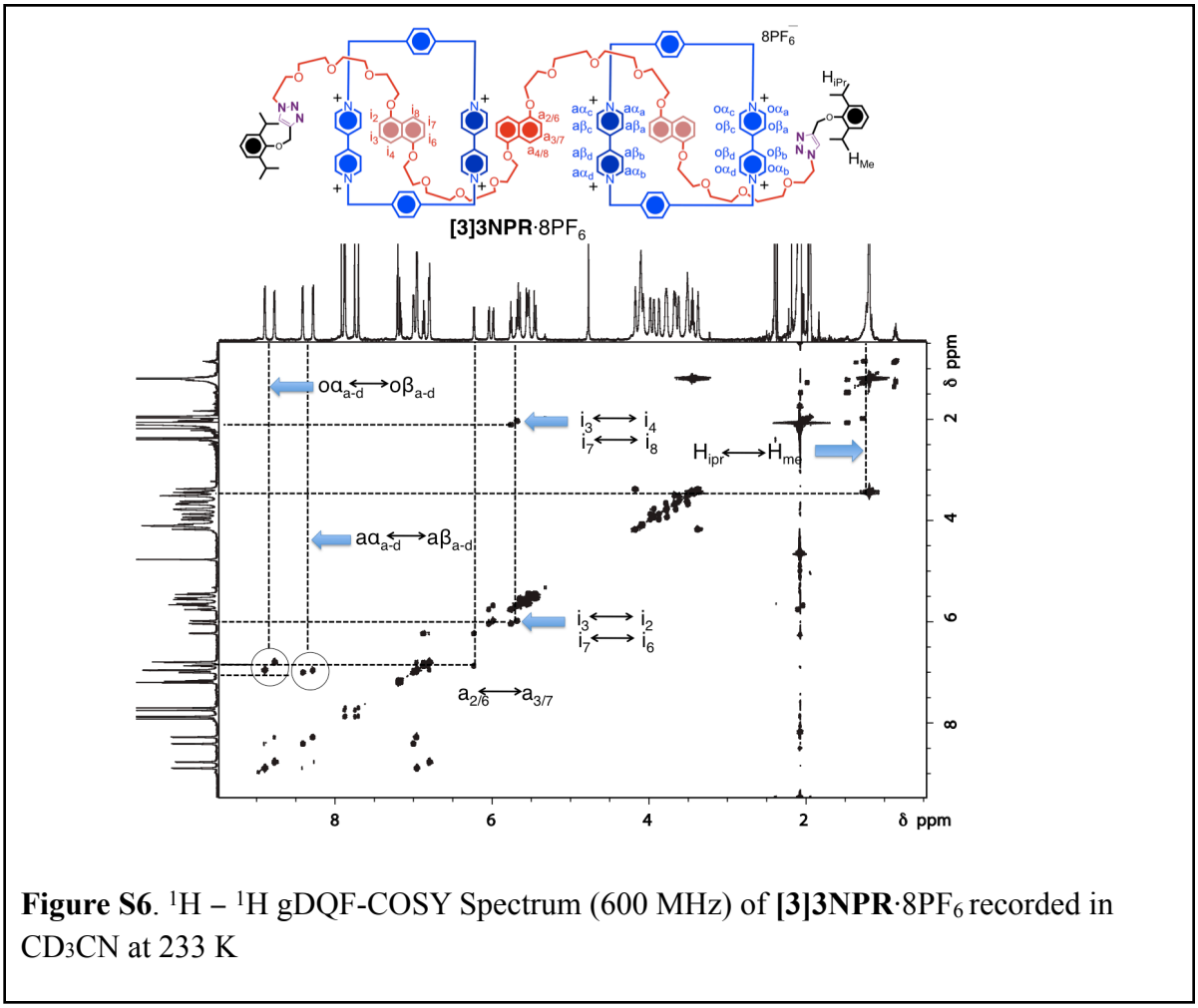


Figure S6. ^{1}H – ^{1}H gDQF-COSY Spectrum (600 MHz) of **[3]3NPR**·8PF$_6$ recorded in CD$_3$CN at 233 K

The ^{1}H-^{1}H gDQF-COSY of **[4]3NPR**·12PF$_6$ (Figure S7) in CD$_3$CN at 233 K showed six sets of α and β protons arising from the CBPQT^{4+} ring – all of which are denoted as 'o', since none of them have an alongside interaction with the DNP units. The known association of the oα protons (a-f) allowed for easy assignment of the corresponding oβ signals as labeled in Figure S7. Unlike **[2]3NPR**·4PF$_6$ (Figure S5) and **[3]3NPR**·8PF$_6$ (Figure S6) all DNP subunits are included in the cavity of the CBPQT^{4+} ring, as denoted by the letter 'i'. The chemical shifts of the protons $i_{2/6}$, $i_{3/7}$ and $i_{4/8}$ (of the central NP unit) are different from the DNP recognition units denoted by i_2-i_6 present on the outer DNP unit.

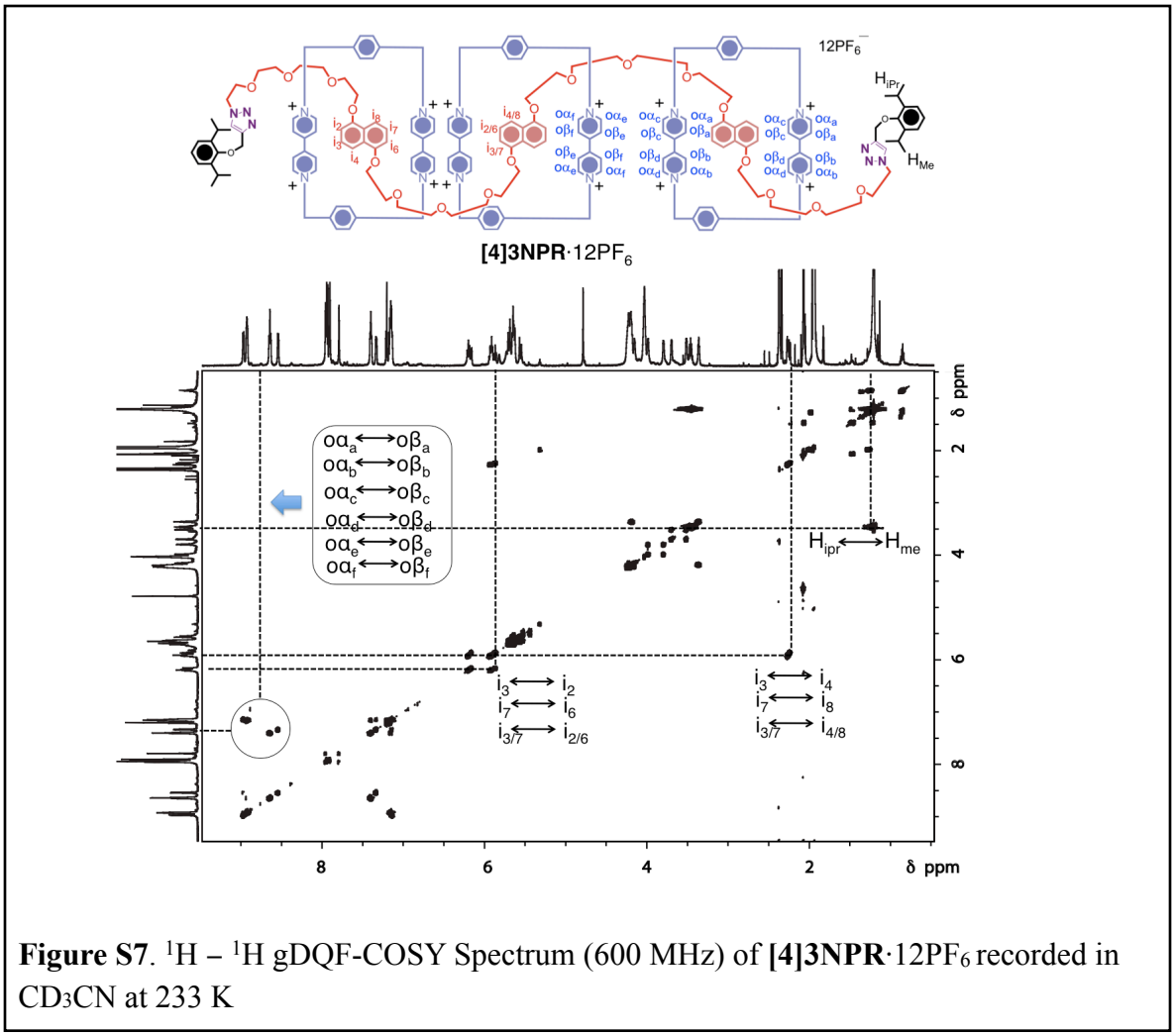


Figure S7. ^{1}H – ^{1}H gDQF-COSY Spectrum (600 MHz) of **[4]3NPR**·12PF$_6$ recorded in CD$_3$CN at 233 K

The ^{1}H-^{1}H gDQF-COSY (Figure S8) of **[4]5NPR**·12PF$_6$ in CD$_3$CN at 233 K reveals six separate doublets for the α and β protons associated with the three CBPQT^{4+} rings, two of which are denoted as 'o'. These signals correspond to the BIPY^{2+} units which face the stoppers (outside) of the rotaxane. The remaining BIPY^{2+} resonances are referred to as 'a' since they demonstrate alongside interactions with the DNP subunits (**Table 1** in the main text). The protons from the DNP subunits are very similar to the **[3]3NPR**·8PF$_6$ in having two sets of signals – included protons (i_1-i_6) which are located inside the cavity of the CBPQT^{4+} ring and the alongside protons (a_1-a_6) that has side on interactions with the BIPY^{2+} subunits. The peaks for the protons $i_{2/6}$, $i_{3/7}$ and $i_{4/8}$ (of the central DNP unit) are different from the DNP recognition units denoted by i_2-i_6 present on the outer DNP unit, as seen in **[4]3NPR**·8PF$_6$.

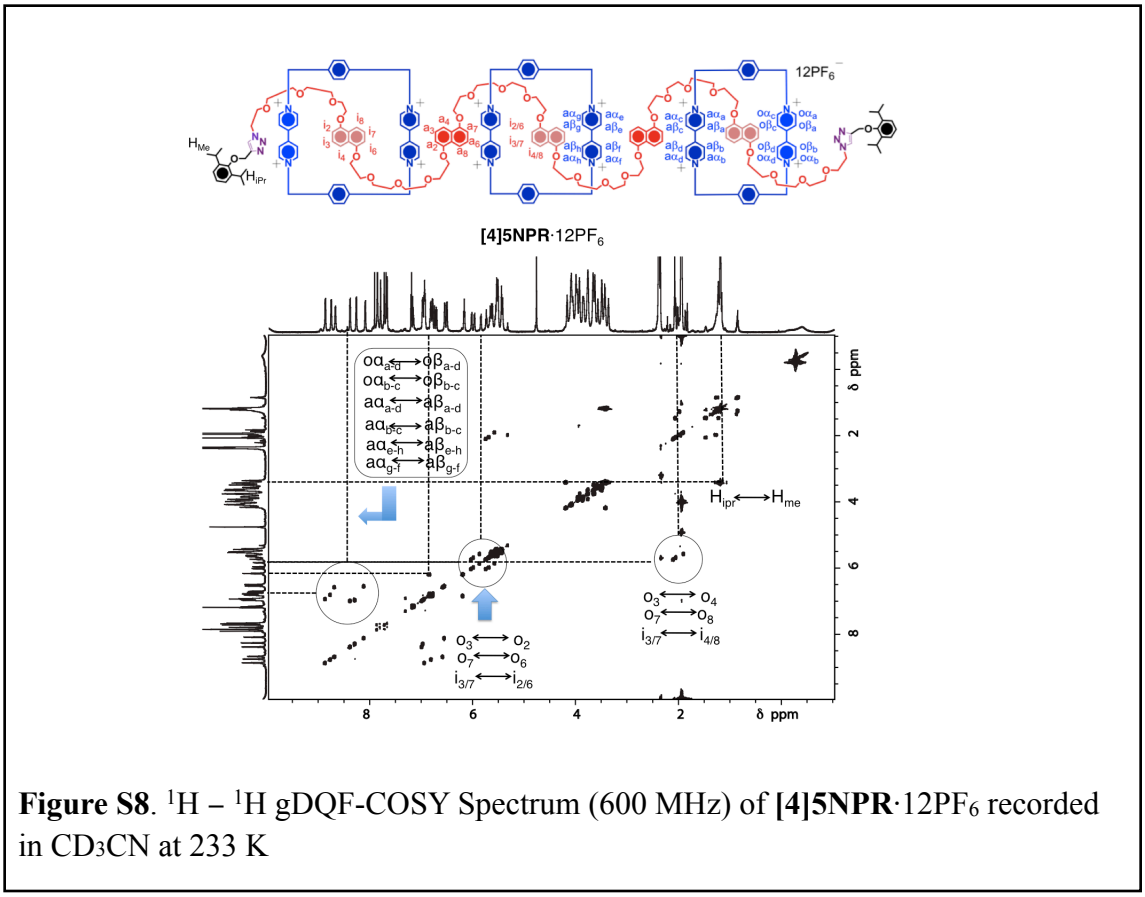


Figure S8. ^{1}H – ^{1}H gDQF-COSY Spectrum (600 MHz) of **[4]5NPR**·12PF$_6$ recorded in CD$_3$CN at 233 K

3C. Nuclear Overhauser Effect Spectroscopy (NOESY)

The ^{1}H-^{1}H gradient-selected NOESY (Figure S9) of **[2]3NPR**·4PF$_6$ in CD_3COCD_3 at 233 K was utilized to further elucidate the solution state structure of these molecule. We focus on the nOe signals between the proton labeled O_6 on the terminal DNP unit and the $a\beta_a$ protons from the CBPQT^{4+} ring. This correlation presents strong evidence for the folded conformation of these donor-acceptor systems in the solution state.

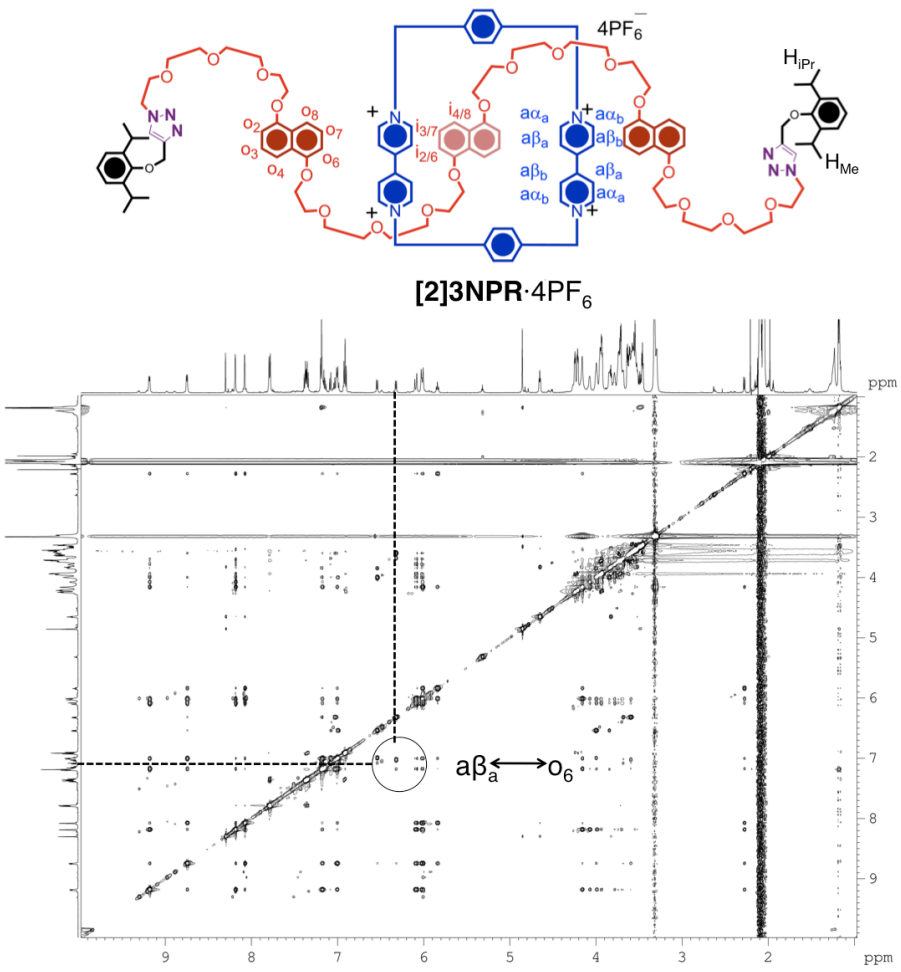


Figure S9. ^{1}H – ^{1}H gNOESY spectrum (600 MHz) of **[2]3NPR**·4PF$_6$ recorded in CD_3COCD_3 at 233 K

The $^{1}H–^{1}H$ gradient-selected NOESY (Figure S10) of **[3]3NPR**·8PF_6 in CD_3COCD_3 at 233K provides further evidence for a folded conformation, similar to that for **[2]3NPR**·4PF_6. We focused on the nOe correlation between the O_6 of the terminal DNP unit and aβ_a protons arising from the $CBPQT^{4+}$ ring. This correlation presents strong evidence for the folded conformation of the molecule in the solution state.

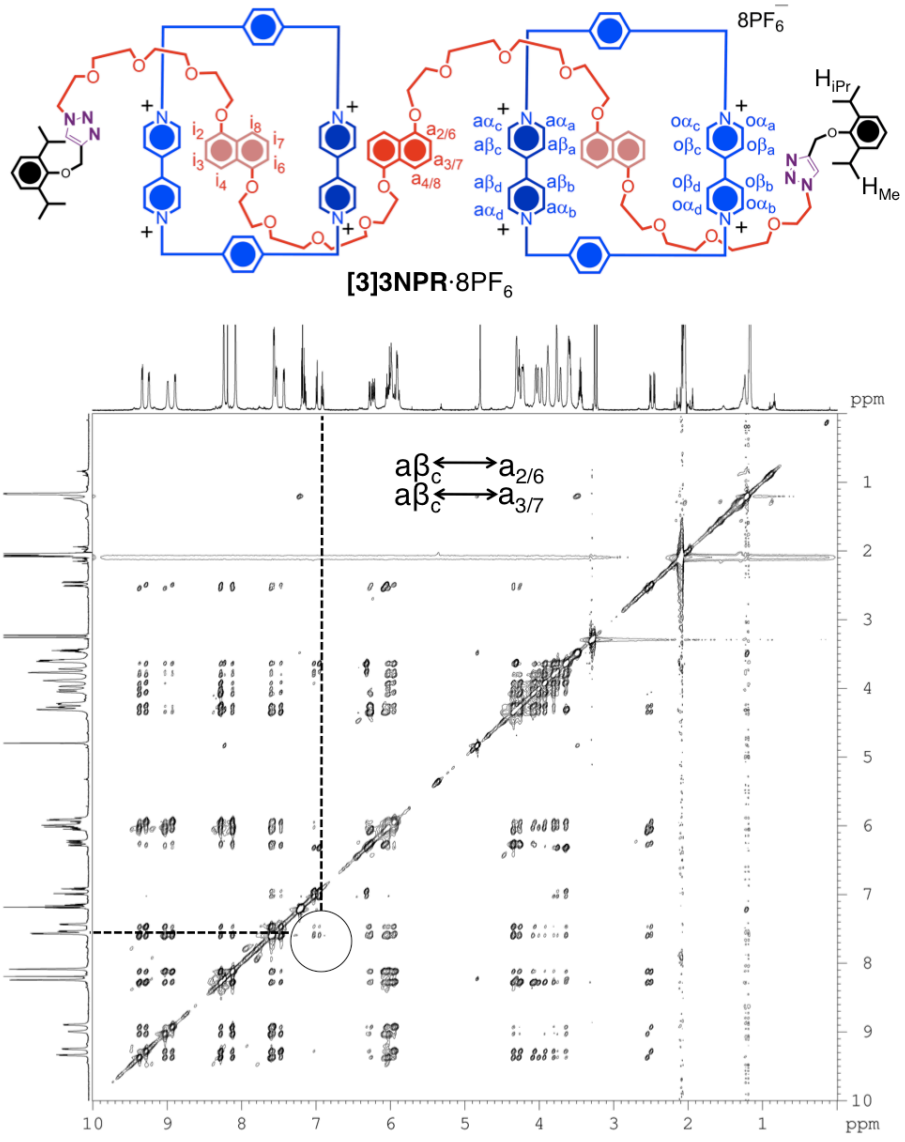
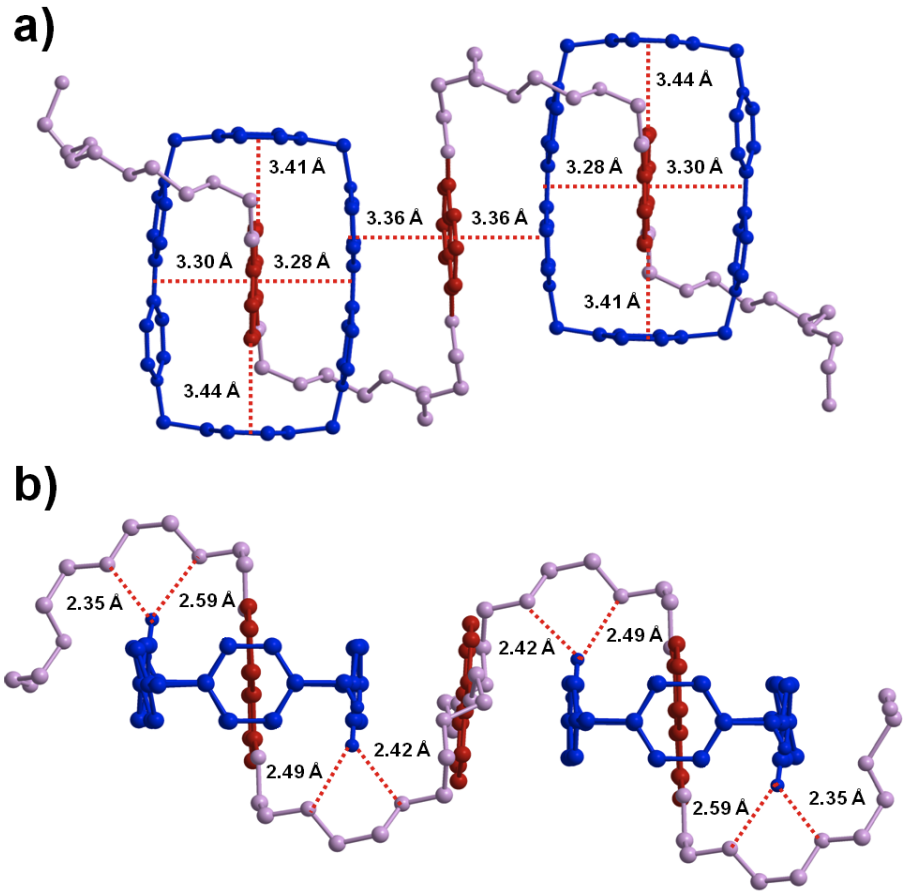


Figure S10. ^{1}H – ^{1}H gNOESY Spectrum (600 MHz) of **[3]3NPR**·8PF_6 recorded in CD_3COCD_3 at 233 K

X-Ray Crystallography

Slow vapor diffusion of iPr_2O into a MeCN solution of 3NP⊂(**CBPQT**·$4PF_6$)$_2$ at 298 K afforded deep purple single crystals suitable for X-ray crystallographic analysis (Figure S12). 3NP⊂(**CBPQT**·$4PF_6$)$_2$ is stabilized by intermolecular noncovalent [π···π], [C–H···π] and [C–H···O] interactions (Figure S11b). The face-to-face [π···π] interplanar separations (Figure S11a) between the inside DNP unit and the center of the outside



S11. A ball-and-stick representation of the X-ray crystal superstructure of 3NP⊂(**CBPQT**·$4PF_6$)$_2$ illustrating (a) the face-to-face [π···π] and the edge-to-face [C–H···π] noncovalent bonding distances between the $CBPQT^{4+}$ rings (blue) and the DNP units (red) and (b) the [C–H···O] distances between the oxygen atoms of the tetraethylene glycol thread and the $CBPQT^{4+}$ rings.

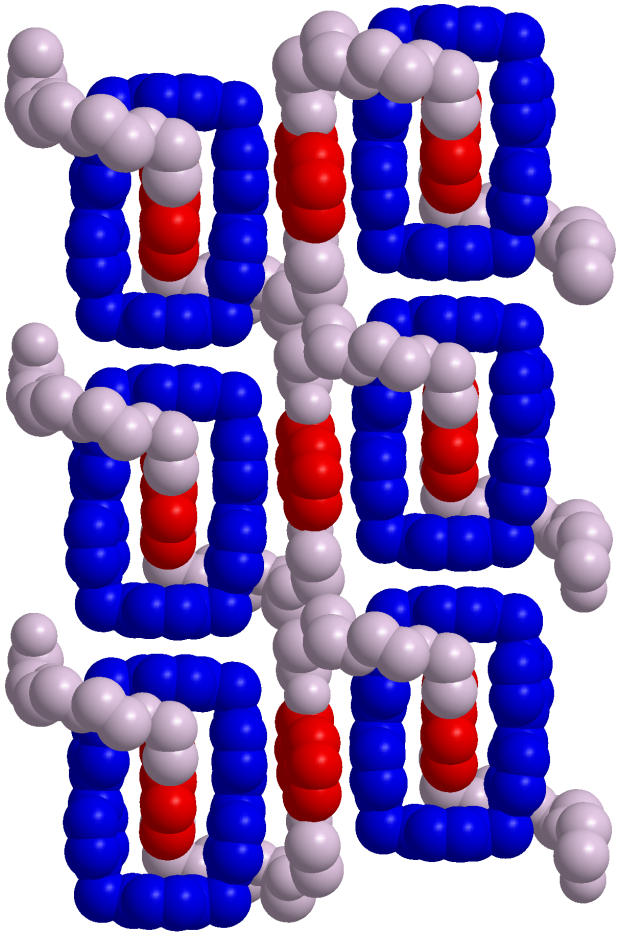


Figure S12. A space-filling representation of the packing of the [3]pseudorotaxane 3NP⊂(**CBPQT**·4PF_6)$_2$ in the solid-state, illustrating noncovalent face-to-face [π···π] interactions between the *p*-xylylene of the $CBPQT^{4+}$ rings.

$BIPY^{2+}$ unit and the inside one is 3.30 Å and 3.28 Å respectively. The distance between the middle DNP unit and the inside $BIPY^{2+}$ unit is 3.36 Å. The edge-to-face [C–H···π] interactions between the inside DNP units and the *p*-xylylene of the $CBPQT^{4+}$ ring (3.41 Å and 3.44 Å, see Figure S11a) further stabilize the folded superstructure in the solid state. Upon closer examination of the solid-state crystal superstructure of the [3] pseudorotaxane 3NP⊂(**CBPQT**·4PF_6)$_2$, it can be observed (Figure S11b) that 8 [C–H···O] interactions exist between the $CBPQT^{4+}$ rings and 3NP adding further stability to the folded conformation of the pseudorotaxane. The solid-state packing (Figure S12) of

3NP⊂(**CBPQT**·4PF_6)$_2$ is mediated by noncovalent face-to-face [π···π] interactions between the *p*-xylylenes of the $CBPQT^{4+}$ rings.

X-Ray Crystal Data. The X-ray crystal data for compound 3NP⊂(**CBPQT**·4PF_6)$_2$ was collected at 173 K using a Rigaku 007HF RA generator (Cu-K_α radiation) equipped with confocal optics and Saturn 944+ CCD system. Intensities were corrected for Lorentz-polarization and for absorption. The superstructure was solved by direct methods. Hydrogen atoms bound to carbon were idealized. Structural refinements were obtained with full-matrix least-squares based on F^2 by using the program SHELXTL. CCDC 769519 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

Crystal data for 3NP⊂(**CBPQT**·4PF_6)$_2$: 2($C_{62}H_{84}O_{20}$)4($C_{36}H_{32}N_4$)16(F_6P)24(C_2H_3N)O, M = 2142.80, space group *C 2/c*, monoclinic, a = 23.1974(12), b = 14.9199(8), c = 51.042 (3) Å, α = 90.00 °, β = 100.175(2)°,γ = 90.00°, U = 17387.9 Å^3, Z = 2, Z' = 0, μ = 2.427 mm^{-1}, 126248 reflections collected, 11023 observed independent reflections (R_{int} 0.0854) gave R 0.1969 for I > 2σ(I) and $wR(F^2)$ was 0.5261.

Computational Methods: Calculations were performed on all systems using density functional theory (DFT) with the M06-L and M06-2X functionals, as implemented in Jaguar 7.6. Starting with a structure from the crystallographic data we optimized the geometry using the 6-31G** basis set with the M06-L functional in the gas phase. Single

point energies were calculated using the M06-2X functional and the 6-311++G** basis set. Solvent corrections were based on single point self-consistent Poisson-Boltzmann continuum solvation calculations for acetonitrile (å = 37.5, R_0= 2.18 Å) using the PBF module in Jaguar.

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[S2] P. S. Shirude, V. A. Kumar, K. N. Ganesh, *Eur. J. Org. Chem.* **2005**,(24), 5207−5215.

[S3] W. Zhang, W. R. Dichtel, A. Z. Steig, D. Benítez, J. K. Gimzewski, J. R. Heath, J. F. Stoddart, *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 6514−6519.